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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LEM	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. Publisher.

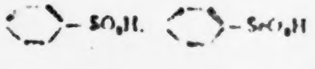
INVESTIGATION OF ORGANIC DERIVATIVES OF SELENIOUS AND TELLUROUS ACIDS AS ANALYTICAL REAGENTS

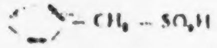
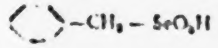
Corresponding Member I. P. Alimarin and V. S. Sotnikov

Up to the present time, investigators have given a great deal of attention to the study of organic reagents containing the functional groups $-COOH$, $-OH$, $=NOH$, $-SH$, $-NH_2$, and others. Organic compounds with arsenic-, sulfur-, and, particularly, phosphorus-containing groups have been considerably less studied.

Furthermore, organic reagents containing the groups $-AsO_3H_2$ and $-PO_3H_2$ are of very great interest from an analytical point of view, as has been shown in a number of works [1-18].

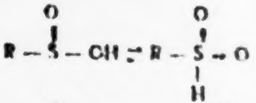
Organic compounds containing $-SeO_2H$, $-SeO_3H$, $-TeO_2H$, and $-TeO_3H$ groups have not yet been studied with the aim of using them for quantitative analysis. In the literature there is only the brief remark by Feigl [8] that benzeneseleninic acid forms slightly soluble precipitates with tetravalent elements, and that this reagent could be used for analytical purposes. Feigl also remarked that, of the reagents containing a sulfinic or seleninic group, only those in which the acid group is directly joined to the aromatic nucleus



are capable of precipitating tetravalent metals, and the presence of a CH_2 group, as in  or , prevents precipitation.

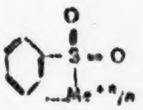
This assertion proved to be incorrect. Both types of reagents can precipitate the ions enumerated below from acid solutions, the difference lying in the somewhat greater solubility of compounds containing a CH_2 group (see Table 3).

Feigl also considers that benzenesulfinic acid can tautomerize [1, 18]



$$\underset{\text{(I)}}{R-\overset{\overset{\displaystyle O}{\|}}{S}-OH} \rightleftharpoons \underset{\text{(II)}}{R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\rightarrow O}$$

and on the basis of these ideas he ascribes to the compounds formed the following structure:

 (Me = Ti^{+4}, Zr^{+4}, Th^{+4})

However, our investigation showed that the first structure reacts, and the compounds formed are typical salts of the corresponding acids, insoluble in organic solvents (ethyl ether, chloroform, etc.).

The conclusion of Feigl as to the ability of cerium (IV), in acid solution, to form a precipitate with benzenesulfinic acid was also shown to be incorrect. As a matter of fact, as was established by us, in the reaction of cerium (IV) with benzenesulfinic acid there is an oxidation-reduction reaction resulting in the reduction of cerium (IV) to cerium (III) and the oxidation of benzenesulfinic acid ($R-SO_2H$) to benzenesulfonic acid ($R-SO_3H$); in addition, a disulfone $(RSO_2)_2$ is formed as a white, flocculent precipitate. The trivalent cerium quantitatively remains in solution.

A similar precipitate is also formed by the action of other strong oxidizing agents.

Benzeneseleninic acid is less prone to oxidize, and, therefore, it forms a precipitate with cerium (IV).

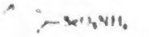
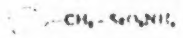
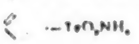
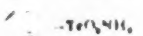
We synthesized and were the first to investigate the class of organic derivatives of selenous acid containing the function-analytical group $-SeO_2H$, methane-, ethane-, propane-, butane-, benzene-, and naphthaleneseleninic acids, and also the series of organic derivatives of selenous acid containing various substituents, o-nitro-, p-nitro-, o-carboxy-, p-methylbenzeneselenic acids, etc.

Moreover, benzylsulfinic, benzylseleninic, and benzenetellurinic acids were synthesized and investigated.

Organic compounds of this type, owing to the presence of the inorganic acid group $-SeO_2H$ or $-TeO_2H$, react in neutral or weakly acid solutions with many elements (see Table 1) with the formation of slightly soluble compounds.

TABLE 1

Results of Qualitative Reactions of Organic Derivatives of Selenous and Tellurous Acids with Inorganic Ions in Neutral or Weakly Acid Medium*

Reagent	Elements																		
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$C_6H_5-SeONH_4$		+					+	+	+	+	+	+	+	+	+	+	+		
$C_6H_5\ SeO_2NH_4$		+	-				+	+	+	+	+	+	+	+	+	+	+		
 $-SeO_2NH_4$				-	—	—	+	+	+	+	+	+	+	+	+	+	+	-	-
$-SeO_2NH_4$	+	+	—		—	-	+	+	+	+	+	+	+	+	+	+	+	+	-
$O_2N-\ -SeO_2NH_4$		+	—			-	+	+	+	+	+	+	+	+	+	+	+		
$H_3C-\ -SeO_2NH_4$		+	-	-	—	—	+	+	+	+	+	+	+	+	+	+	+	+	-
 $-CH_2-SeO_2NH_4$					-	-	+	+	+	+	+	+	+	+	+	+	+	-	—
 $-TeO_2NH_4$	—	+	-	—	-	-	+	+	+	+	+	+	+	+	+	+	+	-	—
SeO_2NH_4	-	—		—	—	—						-		—	-		·	-	—
 $-TeO_2NH_4$		-	-	-	—	—	-	-	—	—	—	—	-	-	-	-	·		-

Note. A + sign indicates the formation of a precipitate, a - sign indicates no precipitate.

---

* This table demonstrates the possibility of a number of determinations and separations of elements, concerning which we have reported in other papers of ours. Copper, silver, lead, and cobalt precipitate with a large excess of the reagent

On the contrary, metallic salts of aromatic seleno acids ($R-SeO_3H$) and the similar salts of telluro acids ($R-TeO_3H$) are readily soluble in water, therefore, benzeneselenonic and benzenetelluronic acids cannot have any widespread application in analysis.

TABLE 2

Dependence of the Sensitivity of the Reaction in Detecting Various Ions on Molecular Weight of the Reagent

Reagent	Molecular weight	Sensitivity of the reaction, γ, ml			
		Fe(III)	Bi	Ti	Zr
$(NH_4)_2SeO_3$	163	10.1	9.4	4.4	3.3
C_3H_7—SeO_2NH_4	172	7.8	–	—	—
C_6H_5—SeO_2NH_4	206	2.7	2.6	1.3	1.0
$C_{10}H_7$—SeO_2NH_4	256	1.5	1.4	1.0	0.7

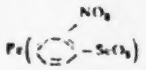
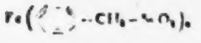
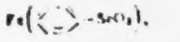
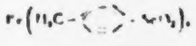
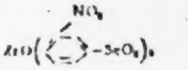
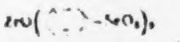
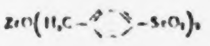
TABLE 4

Results of the Potentiometric (a) and Amperometric (b) Determination of Bismuth

Bi present, mg	Found Bi, mg	
	a	b
16.90	16.92	—
16.90	16.93	—
8.45	8.44	—
8.45	8.45	—
4.23	4.23	4.23
4.23	4.24	4.22
2.12	—	2.10
2.12	–	2.11

TABLE 3

Solubility of Iron and Zirconium Benzeneseleninates in Water

Compound	Solubility, moles/liter
	4.4 · 10 [illegible]
	5.6 · 10 [illegible]
	4.0 · 10 [illegible]
	3.4 · 10 [illegible]
	1.4 · 10 [illegible]
	1.2 · 10 [illegible]
	9.8 · 10 [illegible]

Of the group of reagents synthesized, the most interesting for analytical purposes are the aromatic derivatives of selenous acid, benzene- and naphthaleneseleninic acids, since they quantitatively precipitate from acid solutions the tetravalent elements titantium, zirconium, hafnium, thorium, cerium, tin, and also niobium, tantalum, bismuth, and iron (III).

The selectivity of the action of benzene- and naphthaleneseleninic acids can be increased by regulation of the pH and by the use of complexing agents.

An investigation showed that zirconium ammonium benzene- and naphthaleneseleninates are quantitatively precipitated from strongly acid solutions, for example, 2.0 N HNO_3. The majority of other elements are not precipitated, and do not interfere with the determination of zirconium, exceptions being tin (IV), titanium, niobium, tantalum, and tetravalent cerium which form similar precipitates in strongly acid solution.

TABLE 5

Results of the Determination of Zirconium in Eudialyte and of Titanium in Titanomagnetite by the Benzene- (a) and Naphthaleneseleninate (b), Phenylarsonate (c), and Cupferronate (d) Methods

Element	Found MeO_2			
	a	b	c	d
ZrO_2	10.3[illegible] 10.34	10.30 10.28	10.31 [illegible]	
TiO_2	41.83 41.74	41.97 41.69	–	41.80 41.78

The effect of the last four elements can easily be eliminated by the addition of hydrogen peroxide, which forms complex compounds with them and prevents their precipitation (in acid medium, cerium is reduced by hydrogen peroxide to the trivalent state, and the latter does not form insoluble compounds with ammonium benzene- or naphthaleneseleninates). Tin (IV) must be preliminarily removed by precipitation with hydrogen sulfide.

In Table 3 are presented the results of solubility determinations on certain compounds using as indicators the radioactive isotopes iron (59) and zirconium (95).

The compositions of these compounds were established by chemical analysis of the dried precipitates.

It should be noted that selenous acid has already been used in analytical chemistry for the separation and determination of zirconium [13, 14], titanium [15], bismuth [15], niobium, tantalum, and zirconium [16], and telluric acid has been used for the determination of bismuth [17], etc.

However, the organic derivatives of these acids are more valuable analytical reagents, since they possess greatest sensitivity and selectivity of action, especially with the simultaneous use of masking complexing agents.

We developed new gravimetric and physicochemical methods for the determination of tetravalent elements, titanium, zirconium, etc., and also of bismuth and iron (III) in the presence of other elements in industrial and natural materials using ammonium benzene- and naphthaleneseleninates (Tables 4 and 5).

The principle of the amperometric and potentiometric methods was based on the precipitation of the element with benzeneseleninic acid with subsequent solution of the precipitate in mineral acid and iodometric titration of the benzeneseleninic acid.

$$Bi(NO_3)_3 + 3C_6H_5SeO_2H = Bi(C_6H_5SeO_2)_3 + 3HNO_3$$

$$2C_6H_5SeO_2H + 6KI + 6HNO_3 = (C_6H_5Se)_2 + 3I_2 + 6KNO_3 + 4H_2O$$

$$Bi \approx 9I \approx 9Na_2S_2O_3$$

In conclusion, it is necessary to point out the possibility of radiometric titration, using radioactive isotopes, of these elements or of organic compounds containing radioisotopes of selenium or tellurium.

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ELECTROLYSIS OF $CaO-Al_2O_3-SiO_2$ MELTS

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(Presented by Academician I. P. Bardin, October 2, 1956)

Literature data on the electrolysis of $CaO-Al_2O_3-SiO_2$ melts are few. Thus, Bockris and co-authors [1] demonstrated the applicability of Faraday's law during the liberation of oxygen in the form of CO and CO_2 at a carbon anode in $CaO-SiO_2$ melts. But neither they nor Martin and Derge [2], who passed an electric current through $CaO-Al_2O_3-SiO_2$ slags, observed any cathode products. It is possible that this was due to the low specific gravity of Si, Al, and Ca, their appreciable vapor pressure and high chemical activity, and the formation of ions in a lower state of oxidation.

In order to collect the products of the cathode process, we used as cathodes liquid cast iron (4.5% C) and copper, which have the ability to dissolve, first, Si and Al and, second, Ca, Mg, and Fe. The experiments were carried out as previously described [3] in a fused magnesium cell having anode (h = 40-45 mm; d = 15-18 mm), central (h = 55 mm; d = 7 mm), and cathode (h = 65 mm; d = 7 mm) compartments connected by narrow channels (d = 2-3 mm). Current to the cathode, which weighed from 3 to 8 g, was carried below by tungsten or molybdenum wires. The anodes were carbon rods. On the bottom of the center compartment was placed a "guard" (liquid cast iron or copper), which controlled the process in the absence of current. The amount of electricity passed was measured by a copper coulometer. The current efficiency was determined by determining the composition and weight of the cathode and "guard."

TABLE 1

Results of Experiments on the Electrolysis of $CaO-Al_2O_3-SiO_2$ Melts

Slag composition, %				Temperature, °C	Current density, amp/sq.cm.	Current passed amp.-hr.	Cathode material	Current efficiency, %		
SiO_2	Al_2O_3	CaO	MgO					Si	Al	Overall
6.5	39.4	46.6	7.1	1385	1.20	0.90	Cast iron	63.9	13.9	80.8
6.4	41.3	46.6	6.1	1370	1.03	0.95	Copper	68.1	15.1	83.2
6.3	41.0	46.2	5.9	1380	1.17	0.72	Cast iron	71.0	14.3	85.3
16.9	28.8	45.4	7.5	1390	1.17	0.87	Copper	47.2	11.0	58.2
17.2	28.9	45.9	7.2	1375	1.29	1.11	Cast iron	48.3	9.6	57.9
36.5	11.0	43.9	8.0	1370	2.47	0.59	Cast iron	39.7	4.5	44.2
38.0	11.0	44.5	7.0	1390	1.17	1.02	Cast iron	39.5	4.2	43.7
38.2	10.8	44.0	6.8	1380	1.17	1.17	Copper	38.7	3.6	42.3
38.7	18.5	35.0	8.3	1390	1.81	1.25	Cast iron	41.0	7.9	48.9
39.2	18.6	35.2	7.2	1370	1.17	1.51	Cast iron	40.1	7.2	47.3
55.5	11.0	20.7	12.2	1380	1.29	0.80	Cast iron	57.3	4.8	62.1
56.1	13.2	21.0	11.1	1390	1.29	0.79	Copper	59.2	5.3	64.5
0.2	46.3	47.2	6.1	1440	1.81	0.82	Cast iron	-	21.0	21.0

Notes. 1) The data are for cathode compartments with h/d = 7.5-8.0. 2) Content of iron oxides in the slags exceed 0.15% *3. Magnesium oxide was introduced into the slag to decrease corrosion of the walls of the electrolysis cell.

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* As in original – Publisher's note.

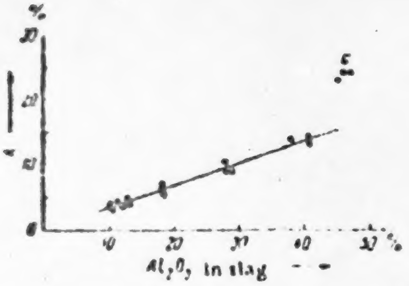

Fig. 1. Variation in the current efficiency (A) for aluminum with Al_2O_3 content of the slags at a cathode compartment h/d of 8 (point 5 a for a melt of 11% CaO, 41% Al_2O_3, 6% MgO).

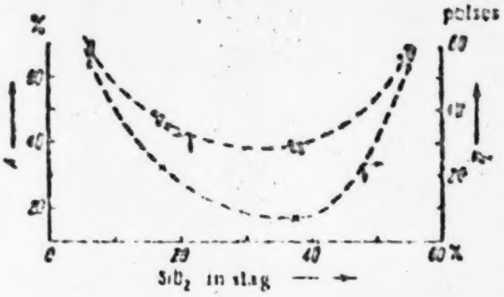

Fig. 2. Current efficiences for silicon (A) and viscosity (η) of $CaO-Al_2O_3-SiO_2$ melts for cells with h/d = 8.

As seen from the data of Table 1, the data of which relate to cells with closely similar dimensions, the major product of the electrolysis of the $CaO-Al_2O_3-SiO_2$ melts was silicon. Its current efficiency varied in the limits of 38 to 71%, while for Al it was appreciably less and did not exceed 24%. The over-all current efficiency varied from 42 to 90%, frequently far from 100%.

In order to determine which unconsidered process consumed the remaining part of the electricity passed, we compared the relations of the current efficiencies for Al and Si to their content in the slag. As Fig. 1 shows, the current efficiency for aluminum increased regularly with the Al_2O_3 content of the melt. On the contrary, the current efficiency for silicon first decreased from 71 to 38% and then increased to 59% as the SiO_2 content was increased. The minimum corresponds to the slag with the lowest viscosity. Figure 2 illustrates this parallelism between the current efficiency for silicon and the literature values [4-6] of melt viscosities. Hence, it follows that the decrease in current efficiency was dependent on a process whose rate was determined by diffusion of some of the molecules in the electrolyte.

In support of this is the regular decrease in current efficiency for silicon with an increase in temperature and, therefore, a decrease in viscosity. Thus, for a slag having the composition 30% CaO, 18% Al_2O_3, 39% SiO_2, and 7% MgO, the current efficiency was 52% at 1290°, 45% at 1350°, and 41% at 1380°. Further evidence of this is found in the increase in current efficiency for Si with an increase in the ratio of the height (h) of the cathode compartment to its diameter (d) (Fig. 3). The latter circumstance indicates oxidation by the furnace atmosphere of the particles, which decreases the current used.

These particles are not only Fe^{3+} ions, since reduction of them to Fe^{2+} at the cathode and regeneration at the boundary with the gas phase [3] could hardly appreciably effect current efficiency owing to the low content of iron oxides in the melts (up to 0.15%) and the high current density (up to 6 amps/cm^2). As regards the Mg^{2+} and Ca^{2+} ions, their reduction to monovalent ions seems improbable under the conditions used. To some slight extent, perhaps, this should be considered in connection with the formation of subcompounds of Al [7]. To this should be added that we did not generally detect calcium in the copper cathodes, and the current efficiency for magnesium was very low and did not exceed 3-4%. Finally, the possibility that the current efficiencies for them was somewhat higher cannot be excluded, since they could have been lost by vaporization.

TABLE 2

Anodic Solution of Silicon in $CaO-Al_2O_3-SiO_2$ Melts

Slag composition, %				Temperature, °C	Anode composition before the experiments*	Current density, amps/sq. cm.	Current passed, amp.-hr.	Current efficiency, %
CaO	Al_2O_3	SiO_2	MgO					
35.8	18.3	[illegible]	7.4	1340	Fe – Si (21.3)	1.03	1.72	104.0
44.2	11.3	37.9	6.[illegible]	1340	Fe – Si (21.3)	1.17	1.35	80.2
43.9	11.0	[illegible]	8.0	1370	Fe – Si (21.3)	1.03	1.17	91.0
48.2	36.7	[illegible]	7.0	1370	Fe – Si (21.3)	1.20	0.70	97.5
29.7	13.0	55.2	12.2	1380	Fe – Si (21.3)	1.03	0.83	95.3
47.0	40.2	9.2	7.0	[illegible]	Cu – Si (17.5)	1.03	0.93	98.3
48.2	11.0	[illegible]	7.[illegible]	[illegible]	Cu – Si (17.5)	1.17	1.12	103.2

* In parentheses, % Si.

Apparently, the most probable competetive process is overcharging of the silicon ions

$$Si^{4+} + 2e \rightarrow Si^{2+}$$

The existence of divalent silicon ions in slags has been shown by a large number of observations [8], and the possibility of overcharging is indicated by the form of the corresponding polarization curves [9]

The comparatively rapid diffusion of divalent silicon to the surface of the catholyte and its oxidation there to the tetravalent form by the furnace atmosphere prevented development of the process $Si^{2+} + 2e \rightarrow Si$ and thereby decreased the current efficiency for silicon.

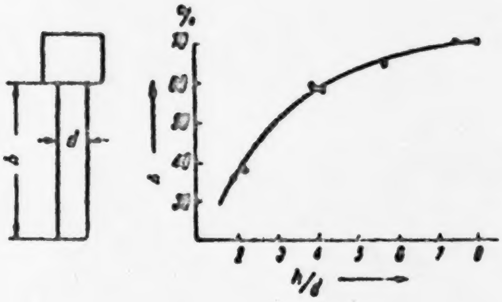

Fig. 3. Variation in current efficiency (A) (for Si) with h/d of the cathode compartment for a slag of the composition 47% CaO, 41% Al_2O_3, 6% SiO_2, and 6% MgO at 1380°.

The lower current consumption during discharge of Al and Mg in comparison to Si is in qualitative agreement with the high stability of these oxides, more precisely, with the increasing value of the standard isobaric potential calculated taking into account the energies of the bonds of these oxides with the melt and the heats of formation of intermetallic compounds with the cathode (FeSi, Cu_2Mg, etc.).

In conclusion, we present data on the anodic solution of silicon from the alloys Fe – Si (21.3% Si) and Cu – Si (17.5% Si) in slags of various compositions (Table 2).

As Table 2 shows, anodic solution proceeds at current efficiencies of 90 to 104%. This, and also the possibility of obtaining high cathode current efficiencies, attests to the applicability of Faraday's law during electrolysis of CaO – Al_2O_3 – SiO_2 melts.

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REDUCTIVE DIMERIZATION OF DERIVATIVES OF α, β -UNSATURATED ACIDS

Academician I. L. Knunyants and H. S. Vyazankin

It has previously been established [1] that the major product of the direct electrochemical reduction of acrylonitrile under specific conditions is adiponitrile. Since this method of reductive dimerization is distinguished by highly reproducible results and permits reduction to be carried out under comparable conditions in the presence of different amalgams, it is possible to study the dependence of the phenomenon of hydrodimerization on the structures of the reducible compounds and the nature of the amalgams.

With this aim, the reductive dimerization of a series of derivatives of α, β - unsaturated acids was carried out.

The reductive dimerization was carried out in an apparatus which was a combination of an electrolyzer, for the preparation of the amalgams, and a reaction cell, in which the amalgam reacted with the reaction mixture (Figure 1). The surface area of the mercury cathode was 1.80 sq. dm, while the surface area of the amalgam in the reaction cell was 2.35 sq. dm. The amalgams were prepared by electrolysis of 40% solutions of sodium or potassium hydroxides and a saturated solution of LiCl at a current flow of 8-9 amps. and a temperature of 14-16°. The reaction mixture consisted of the reducible substance and 20% HCl (1 : 2.5 mole). The reaction was interrupted when the mixture became alkaline toward phenolphthalein.

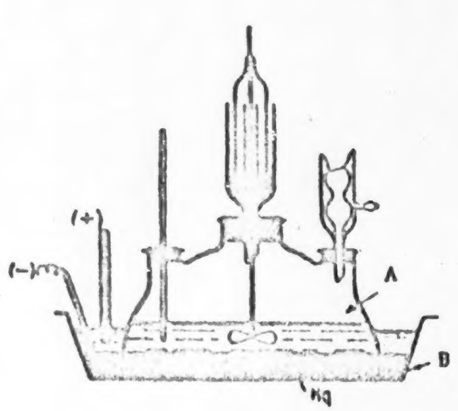
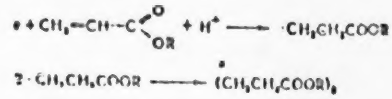


Fig. 1. A) reaction cell, B) electrolyzer

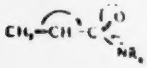
The investigation showed that one of the factors affecting the formation of hydrodimers is the nature of the conjugated system of the reducible compound. This observation cannot be considered unexpected, if it is assumed that formation of the hydrodimer is preceded by reduction of the molecules to intermediate radicals and subsequent dimerization of the latter according to the scheme:



$$e + CH_2{=}CH{-}C\begin{matrix} \nearrow O \\ \searrow OR \end{matrix} + H^+ \longrightarrow \cdot CH_2CH_2COOR$$

$$2 \cdot CH_2CH_2COOR \longrightarrow (CH_2CH_2COOR)_2$$

It is well known that unconjugated ethylenic bonds are not reduced by amalgams. With styrene and vinyl acetate, we established that conjugation of an ethylenic bond with a benzene ring or with an unshared pair of electrons of the oxygen atom is also not sufficient for reduction of the double bond by lithium or potassium amalgam. In the case of amides and diethylamides of α, β -unsaturated acids, conjugation of the C = C and C = O groups is apparently considerably weakened by the competing conjugation of the unshared pair of electrons of the nitrogen atom with the π- electrons of the C = O bond:



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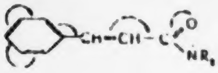
This can also explain the fact that the amides and diethylamides of acrylic and crotonic acids are very difficultly reduced and do not yield hydrodimers, as well as the fact that the amide and diethylamide of methacrylic acid are not reduced.

In the diethylamide and diphenylamide of cinnamic acid, conjugation of the π- electrons of the carbonyl group, the ethylenic bond, and the benzene ring occurs:



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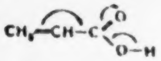
and apparently as a consequence of this, competing conjugation is less developed. It is seen from Table 1 that these compounds yield hydrodimers together with the products of normal reduction.

This is in agreement with the literature data [2] on the hydrodimerization of α, β-unsaturated acids, in which competing conjugation also occurs:



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And in this case, the phenomenon of reductive dimerization is characteristic only for acids in which $C_6H_5-CH_2=CH-$ and similar groups are present in the β-position. The connection between the occurrence of conjugation and the ability to form hydrodimers is also observed in the ethers and nitriles of α, β-unsaturated acids (see Table 1). Thus, for example, diethyl maleate, in which the conjugated system is somewhat disrupted [3], gives hydrodimer in lower yield than does diethyl fumarate. The decrease in yield of hydrodimer in the case of methyl methacrylate and the absence of reduction during hydrogenation of methacrylonitrile with potassium and lithium amalgams can be explained by a decrease in the conjugation of the double bond with the carbonyl group owing to the hyperconjugating effect of the methyl group. In addition, it is seen from the data obtained that other factors can decisively affect reductive dimerization. Thus, the absence of reduction during the treatment of ethyl β, β-dimethacrylate with sodium and potassium amalgams is apparently explained by shielding of the β-position by the two methyl groups. With an increase in the molecular weight of the alcohol radical in the acrylic ester series, the yield of hydrodimer decreases; finally, it is difficult to explain the increased stability of the nitriles of α, β-unsaturated acids toward reaction with amalgams of the alkali metals as compared to the corresponding esters.

TABLE 1

Original compound	Reducing agent	Hydrodimer structure	Yield, %
$CH_2=CHCOOCH_3$	K(Hg)	$(CH_2CH_2COOCH_3)_2$	34.7
$CH_2=CHCOOC_2H_5$	K(Hg)	$(CH_2CH_2COOC_2H_5)_2$	12.0
$CH_2=CHCOOC_3H_7$-n	K(Hg)	$(CH_2CH_2COOC_3H_7$-n$)_2$	24.0
$CH_2=CHCOOC_4H_9$-n	K(Hg)	$(CH_2CH_2COOC_4H_9$-n$)_2$	27.0
$CH_2=C(CH_3)COOCH_3$	K(Hg)	$(CH_2CH(CH_3)COOCH_3)_2$	23.1
$CH_2=C(CH_3)COOCH_3$	Na(Hg)	$(CH_2CH(CH_3)COOCH_3)_2$	16.1
$CH_3CH=CHCOOC_2H_5$	K(Hg)	$(CH_3CHCH_2COOC_2H_5)_2$	71.0
$(CH_3)_2C=CHCOOC_2H_5$	Li(Hg)	$[(CH_3)_2CCH_2COOC_2H_5]_2$ *	31.4
$(CH_3)_2C=CHCOOC_2H_5$	Na(Hg); K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	**
$C_2H_5OOCCH=CHCOOC_2H_5$, cis	K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	7.3
$C_2H_5OOCCH=CHCOOC_2H_5$, cis	Al(Hg)	—	0.0
$C_2H_5OOCCH=CHCOOC_2H_5$, trans	K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	34.6
$C_2H_5OOCCH=CHCOOC_2H_5$, trans	Al(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	12.7
$C_6H_5CH=CHCOOC_2H_5$	K(Hg)	$(C_6H_5CHCH_2COOC_2H_5)_2$	51.3
$CH_2=C(C_2H_5)COOC_2H_5$	K(Hg)	$(CH_2CH(C_2H_5)COOC_2H_5)_2$ *	27.5
$CH_2=CHCN$	K(Hg)	$(CH_2CH_2CN)_2$	60.1
$CH_3CH=CHCN$	Li(Hg)	$(CH_3CHCH_2CN)_2$ *	37.0
$CH_3CH=CHCN$	Na(Hg); K(Hg)	—	**
$(CH_3)_2C=CHCN$	K(Hg); Li(Hg)	—	**
$CH_2=C(CH_3)CN$	K(Hg); Li(Hg)	—	**
$C_6H_5CH=CHCN$	K(Hg)	$(C_6H_5CHCH_2CN)_2$ *	60.0
$C_6H_5CH=CHCN$	Al(Hg)	$(C_6H_5CHCH_2CN)_2$	22.2
$C_6H_5CH=CHCON(C_2H_5)_2$ ***	K(Hg)	$[C_6H_5CHCH_2CON(C_2H_5)_2]_2$ *	23.7
$C_6H_5CH=CHCON(C_6H_5)_2$ ***	K(Hg)	$[C_6H_5CHCH_2CON(C_6H_5)_2]_2$ *	5.2

TABLE 2

Formula	B.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	C, %		H, %		N, %	
					found	calc.	found	calc.	found	calc.
$(CH_2CH_2COOCH_3)_2$	111–113	10	1.4288	1.0642	55.39	55.16	8.00	8.10	—	—
$(CH_2CH_2COOC_2H_5)_2$	113–118	8	1.4233	1.0085	59.13	59.39	9.04	8.97	—	—
$(CH_2CH_2COOC_3H_7$-n$)_2$	152–154	13	1.4301	0.9604	62.75	62.58	9.41	9.63	—	—
$(CH_2CH_2COOC_4H_9$-n$)_2$	141–143	4	1.4375	0.9631	65.32	65.08	10.21	10.14	—	—
$(CH_2CH(CH_3)COOCH_3)_2$	108–112	12	1.4334	1.0118	59.21	59.39	8.83	8.97	—	—
$(CH_3CHCH_2COOC_2H_5)_2$	109–115	4	1.4350	0.9656	62.40	62.58	9.58	9.63	—	—
$((CH_3)_2CCH_2COOC_2H_5)_2$	117–118	2	1.4421	0.9650	64.81	65.08	10.12	10.14	—	—
$(C_2H_5OOCCHCH_2COOC_2H_5)_2$ ****	179–182	4	1.4455	1.4475	55.34	55.48	7.45	7.56	—	—
$(C_2H_5OOCCHCH_2COOC_2H_5)_2$ *****	178–179	3	1.4467	1.4401	55.17	55.48	7.59	7.56	—	—
$(CH_2CH_2CN)_2$	160–162	41	1.4410	0.9528	66.67	66.65	7.61	7.45	25.73	25.90
$(CH_3CHCH_2CN)_2$	121	3	1.4524	0.9524	70.76	70.56	8.71	8.88	20.39	20.56

It follows from our results that the amalgams differ sharply in the ability to reduce derivatives of α, β-unsaturated acids with the formation of hydrodimers. Of the compounds investigated (cf. Table 1), only esters of maleic and fumaric acids and derivatives of cinnamic acid were hydrodimerized by aluminum amalgam in moist ether according to the method of Wilds and Sutton [4] . Among the amalgams of the alkali metals, reactivity increases from sodium amalgam to lithium amalgam, i. e., parallel to the increase in normal potential of these amalgams. In particular, it was possible to carry out with lithium amalgam the reductive dimerization of ethyl β, β-dimethacrylate and crotononitrile, which were not reduced by the other amalgams. Under comparable conditions, with sodium amalgam the yield of hydrodimer was 10-20% lower

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* Compound prepared for the first time.

** Original compound not reduced.

*** Reduction carried out in a 30 % solution of CH_3COOH in alcohol.

**** Prepared by reductive dimerization of diethyl maleate.

***** Product of the hydrodimerization of diethyl fumarate.

Formula	M.p., °C	Solvent for crystallization	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$(C_6H_5CHCH_2COOC_2H_5)_2$	116–117	Alcohol	76.21	76.56	7.41	7.40	—	—
$(CH_3CH(C_6H_5)COOC_2H_5)_2$ *	111–113	Alcohol	[illegible]	76.56	7.51	7.40	—	—
	36–38		76.40	76.56	7.49	7.40	—	—
$(C_6H_5CHCH_2CN)_2$ *	213–215	Acetone	83.31	83.05	6.28	6.20	11.09	10.76
	153–155	Alcohol	82.91	83.05	6.12	6.20	11.01	10.76
$(C_6H_5CHCH_2CON(C_2H_5)_2)_2$	175–177	Alcohol	76.11	76.43	8.74	8.88	6.62	6.86
$(C_6H_5CHCH_2CON(C_6H_5)_2)_2$	288–290	Dimethylformamide	83.78	83.97	6.09	6.04	4.60	4.66

than with potassium amalgam. The structures of the hydrodimers obtained were confirmed by identification of the acids and the formation of the corresponding cyclopentanones from the acids. Investigation showed that reductive dimerization, when it was possible, leads to the formation of a mixture of steroisomers. Hydrodimerization of α-chloroacrylonitrile (cf. Table 1) was accompanied by substitution of hydrogen for the halogen. The reaction products were adiponitrile and propionitrile. Saponification of methyl acrylate paralleled its reductive dimerization, and this sharply reduced the yield of hydrodimer. The properties of the hydrodimers obtained are presented in Tables 2 and 3.

Elementoorganic

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Academy of Sciences USSR

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* See C. B. Translation.

THE REACTION OF BENZYLPYRIDINIUM CHLORIDE WITH CYCLOPENTADIENYLLITHIUM

Associate Member Acad. Sci. USSR D. N. Kursanov, N. K. Baranetskaya
and V. N. Setkina

In the present work, the reaction of cyclopentadienyllithium (I) with benzylpyridinium chloride (II) was studied.

It might be expected that benzylpyridinium chloride would benzylate the cyclopentadiene ring. However, in place of the expected benzyl-substituted cyclopentadiene, a substance (III) was isolated, which had the formula $C_{17}H_{15}N$ on the basis of analytical data and molecular weight determination.

Substance III was a golden yellow crystalline material, stable in air, readily soluble in acetone, nitrobenzene, chloroform and pyridine, less soluble in dioxane, alcohol, and benzene, and insoluble in water, ether, petroleum ether, and carbon tetrachloride.

Compound III decomposed without melting at a temperature above 180°.

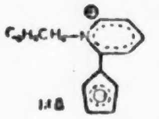
The substance dissolved in dilute acids, and was again precipitated from solution by the action of alkali. With the aim of determining the structure of this compound, we catalytically hydrogenated it over Pt-black in alcohol and in glacial acetic acid at atmospheric pressure [1]. It was found that one mole of III absorbs five moles of hydrogen, which indicated the presence in the molecule of this substance of five double bonds. Determination of the iodine number led to the same conclusion.

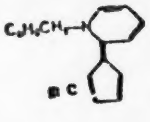
Hydrogenation gave an amine (IV), which was then converted to the chloroplatinate and methiodide, analysis of which corresponded to the formulas $C_{17}H_{23}N \cdot {}^{1}/_{2}\, H_2PtCl_6$ and $C_{18}H_{26}NI$.

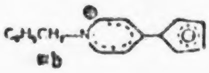
It is known from the literature [2] that the action of alkaline reagents on pyridinium salts frequently leads to cleavage of the pyridine ring at the nitrogen-carbon bond.

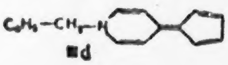
In order to clarify the question of whether the pyridine ring was retained in III, we attempted to acylate amine IV. The presence of a tertiary nitrogen in amine IV would indicate retention of a pyridine ring in substance III, while the presence of a secondary nitrogen would indicate cleavage of the pyridine ring. Experiments showed that amine IV was a tertiary amine, which indicated retention of the pyridine ring in the molecule of III.

The data presented bring into consideration the following structural formulas for substance III.


IIIa


IIIc

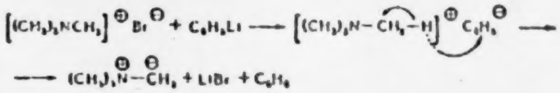

IIIb


IIId

In this connection, it was of interest to obtain experimental confirmation of the polarity of the molecule of substance III. The dipole moment of III was measured for this purpose. The measurement of the dipole moment was performed, at our request, by A. N. Shidlovskaya in the laboratory of Corresponding Member Acad. Sci. USSR Prof. Ya. K. Syrkin, to whom we express our sincere appreciation. The dipole moment was found to be 9.7 D, exceptionally high for an organic compound.

This value of the dipole moment is in sharp nonconformity with the fulvene structure, and confirms the polar nature of our substance which, following the nomenclature proposed by Wittig, must be named benzylpyridinium cyclopentadienylide.

Owing to the work of Wittig [3], it is known that dipolar ions – "ylides" – are formed by the action of phenyllithium on quaternary ammonium salts. Thus, for example, a methylide is formed by the reaction of tetramethylammonium bromide with phenyllithium:



$$\left[(CH_3)_3NCH_3\right]^{\oplus}Br^{\ominus} + C_6H_5Li \longrightarrow \left[(CH_3)_3N-CH_2-H\right]^{\oplus}C_6H_5^{\ominus} \longrightarrow$$

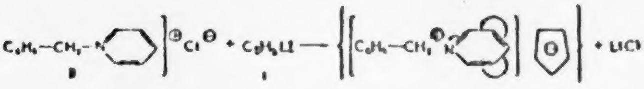
$$\longrightarrow (CH_3)_3\overset{\oplus}{N}-\overset{\ominus}{C}H_2 + LiBr + C_6H_6$$

Moreover, from the work of Schlenk [4] it is also known that the reaction of organosodium and organopotassium compounds with quaternary ammonium salts yields salt-like compounds in which the positively charged ammonium group is ionically bound to a negatively charged hydrocarbon radical. Triphenylmethyltetramethylammonium, benzyltetramethylammonium, etc. are such compounds.

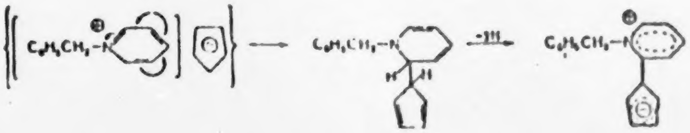
$$(C_6H_5)_3\overset{\ominus}{C}\,\overset{\oplus}{N}(CH_3)_4; \qquad C_6H_5\overset{\ominus}{C}H_2\,\overset{\oplus}{N}(CH_3)_4.$$

Comparing these different cases (the formation of the quaternary salts of Schlenk and the formation of ylides), Wittig was led to the conclusion that the stability of Schlenk's salts depends on the mobility of the hydrogen atoms in the radicals joined to the charged nitrogen atom and also on the proton accepting ability of the anion. In those cases where the cation of the quaternary salt contains a mobile α-hydrogen atom and the anion is a strong proton acceptor, cleavage of the quaternary salt occurs with the formation of an ylide.

In the case investigated by us (the reaction of benzylpyridinium chloride with cyclopentadienyllithium) at first a quaternary ammonium salt of the type of a Schlenk salt is probably formed.



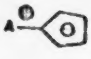
Next, the stable cyclopentadienyl anion alkylates the site of the lowest electron density of the pyridine ring (α - and γ-positions):



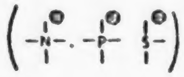
Splitting off of two atoms of hydrogen * (which follows from the analytical data on substance III) then occurs with the formation of the more energy-favorable dipolar compound with a stable cyclopentadienyl anion [5].

Recently, a series of reports has appeared in the literature devoted to dipolar compounds containing a negatively charged cyclopentadienyl radical. Triphenylphosphonium cyclopentadienylide [6], pyridinium cyclopentadienylide [7], and diazocyclopentadiene [8] are such compounds. The unstable ammonium [3, 9] and sulfonium [10] fluorenylides were discovered previously.

They can be generally represented as:



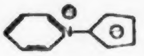
where A is an onium atom.



$$\left(-\overset{|}{\underset{|}{N}}{}^{\oplus}-,\ -\overset{|}{\underset{|}{P}}{}^{\oplus}-\ \ \overset{|}{\underset{|}{S}}{}^{\oplus}-\right)$$

In the majority of cases, this is a brightly colored crystalline material. One will melt at a high temperature, another will decompose, and a third will not melt. They are soluble in polar solvents, and do not dissolve in nonpolar solvents. They dissolve in dilute acids, and are reprecipitated on alkalization. They form salts with alkyl halides (CH_3I, $C_6H_5CH_2Br$, etc.).

Usually, such bipolar compounds are prepared from onium salts by the action of bases which, splitting off a proton from the onium compound, create the opportunity for the formation of a dipolar ion. In all dipolar compounds of this group, the positively charged onium atom is always bound directly to the cyclopentadienyl anion, as can be seen, for example, from pyridinium cyclopentadienylide



The benzylpyridinium cyclopentadienylide obtained by us possesses all of the properties of dipolar ions indicated above. However, in contrast to the previously described dipolar ions of this type, our substance III is the first representative of stable dipolar ions in which a direct bond between the positively charged nitrogen atom and a carbon of the negatively charged cyclopentadienyl nucleus is absent.

EXPERIMENTAL DATA

1. Preparation of cyclopentadienyllithium. To 29.18 g of butyllithium, prepared by the method of Hilman [11], 33.10 g of cyclopentadiene was added dropwise and with stirring. The reaction flask was cooled with ice water during the reaction. After the addition of the cyclopentadiene, stirring was continued for another two hours at room temperature. For the determination of the yield of C_5H_5Li, it was converted to bis-cyclopentadienecarboxylic acid [12]. The yield of C_5H_5Li was 71.9%.

2. Preparation of benzylpyridinium cyclopentadienylide. Into a round-bottomed flask, fitted with a stirrer and reflux condenser, were placed 150 ml of ether and 102.9 g of powdered benzylpyridinium chloride (prepared by the condensation of benzyl chloride with pyridine, then dried and powdered).

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* We did not observe the liberation of hydrogen, probably owing to side oxidation-reduction reactions.

A suspension of cyclopentadienyllithium in ether was added with vigorous stirring to the ethereal suspension of benzylpyridinium chloride. The mixture was stirred for 20 hours at room temperature, after which the reaction products were treated with water. This gave a precipitate, from which 6.55 g of substance III was isolated by crystallization from benzene. From the ether layer was obtained another 12.14 g of III. The total yield was 24.5% of the cyclopentadienyllithium used.*

The molecular weight was 232.0 (cryoscopically from nitrobenzene); calculated for $C_{17}H_{15}N$, 233.3

Found %: C 87.51, 87.43; H 6.47, 6.28; N 5.95, 5.89. $C_{17}H_{15}N$. Calculated %: C 87.52; H 6.48; N 6.01.

3. Investigation of the structure and properties of $C_{17}H_{15}N$.

a. Determination of the iodine number of $C_{17}H_{15}N$. The determination was carried out in chloroform solution. Found: 327.1, 321.2. Calculated for five double bonds, 342.5.

b. Hydrogenation of $C_{17}H_{15}N$. The hydrogenation of the product of the reaction of benzylpyridinium chloride and cyclopentadienyllithium was carried out over Pt-black in alcohol and in acetic acid at atmospheric pressure.

	Sample weight	Amount of hydrogen absorbed	Amount of hydrogen calculated for 5 double bonds
Alcohol	0.5019	232	241
Glacial acetic acid	0.5631	259	270

c. Analysis of salts of the hydrogenated amine. Chloroplatinate, $C_{17}H_{25}N \cdot {}^1/_2H_2PtCl_6$ (decomposition temperature 140°), found % Pt 21.93, 21.82; calculated 21.77. Methiodide, $C_{18}H_{28}NI$ (decomposition temperature 160-170°, found % I 32.82, 33.00; calculated 32.94.

d. Acylation of the hydrogenated amine. Acylation of the hydrogenated amine was carried out on the hydrochloride with acetic anhydride in pyridine medium [13]. Acetic anhydride taken for the acylation 0.3101 g, 0.2446 g; recovered 0.3106 g, 0.2415 g; % error 0.5-1.2. Thus, the acylation data indicate that the hydrogenated amine was tertiary.

e. Determination of the dipole moment of $C_{17}H_{15}N$. The dipole moment, determined by the method of Smals [14], was 9.7 D (in benzene). The experimental error was 2-3%, since the measurement was carried out in highly dilute solution owing to the low solubility of the material. The dipole moment of $C_{17}H_{15}N$ was considerably higher than the usual value for organic compounds.

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* Compound I can be similarly obtained by the reaction of benzylpyridinium chloride with cyclopentadienylpotassium [12] [As in original; apparently compound III is intended here – Publisher's note.]

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* Original Russian pagination. See C. B. translation.

THERMAL TELOMERIZATION OF TRICHLOROSILANE WITH ETHYLENE

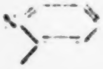
Academician A. N. Nesmeyanov, R. Kh. Freidlina and E. Ts. Chukovskaya

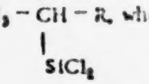
Compounds of silicon which contain an Si – H bond are capable of adding to double and triple bonds of unsaturated compounds. In a previous paper [1], we presented a brief review of such reactions [2-12].

Recently, there has been described the addition of trichlorosilane at the double bond of acrylonitrile, of 2-vinylpyridine, and of allyl cyanide in the presence of organic bases, and an ionic mechanism has been proposed for these reactions [13, 14].

$$Cl_3SiH + B \rightarrow Cl_3Si^- + BH^+$$
$$\overset{\delta+}{C}H_2 = \overset{\delta-}{C}HR + Cl_3Si^- \rightarrow Cl_3SiCH_2\bar{C}HR$$
$$Cl_3SiCH_2\bar{C}HR + BH^+ \rightarrow B + Cl_3SiCH_2CH_2R,$$

where B is an organic base

R = CN, CH$_2$CN, 

Nozakura [14, 15] found that tetrapyridine nickel chloride catalyzes the addition of trichlorosilane to vinyltrichlorosilane, to 1-octene, and to styrene. In all of the cases enumerated, the reaction leads to a mixture of two isomers, $SiCl_3CH_2CH_2R$ and  $CH_3 - \underset{\substack{|\\ SiCl_3}}{CH} - R$, where R = $SiCl_3$, C_6H_{13}, or C_6H_5.

An attempt by us to carry out the telomerization reaction in stainless steel autoclaves using methyldichlorosilane, ethyldichlorosilane, and triethylsilane with ethylene and propylene in the presence of benzoyl peroxide or tertiary butyl peroxide at a temperature of 100-140° and a pressure of 100-300 atm. failed.

We were successful in carrying out the thermal telomerization of methyldichlorosilane with ethylene at a temperature of 260-275° and a pressure of 560 atm. [1].

Under these conditions there was formed a mixture of substances of the structure $CH_3SiCl_2(CH_2CH_2)_nH$, of which compounds for which n = 1-6 were isolated individually.

In the present article, we report on the thermal telomerization of trichlorosilane with ethylene.

The reaction was carried out in a half-liter autoclave of EYa-1T steel. 60 g of trichlorosilane was placed in the autoclave, and, after purging with nitrogen, the ethylene was introduced. The reaction mixture was heated to 285°; the maximum pressure was 200 atm. The reaction was carried out in 2 hours. In this time, the pressure fell to 40 atm. The experiment was repeated 4 times, and the reaction products were combined and subjected to fractional distillation. A total of 261 g of trichlorosilane was used. The weight of the reaction products was 353 g. The product was fractionated in a column having 15 theoretical plates, 10 g of the original trichlorosilane was distilled and then 263 g of individual alkyltrichlorosilanes having the structure $Cl_3Si(CH_2CH_2)_nH$, where n = 1–5. The residue (42 g) was a mixture of higher alkyltrichlorosilanes. The properties and yields of the alkytrichlorosilanes obtained are shown in Table 1.

TABLE 1

$SiCl_3(CH_2CH_2)_nH$

n	Yield		n_D^{20}	d_4^{20}	*MR*		B.p., °C/mm		Source	Si in %	
	in g	in % of total products			found	calc.	our data	Lit.		calc.	found
1	69	20.1%					98	97–100	(16)	—	—
2	87	25.3%	1.4452	1.1577	43.19	42.82	146–147	147–151	(17)	14.65	14.72 14.45
3	54	15.4%	1.4440	1.1094	52.51	52.12	87–89/30	127/38	(18)	12.78	12.83 12.59
4	45	13.1%	1.4490	1.0744	61.76	61.41	96.5/10	119/28 231–232/731	(18)	11.33	11.26 11.67
5*	14	4.0%	1.4547	1.0501	71.17	70.71	76/2	153/84	(18)	10.17	10.55 10.58
n > 5	42	12.2%									

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* For $SiCl_3C_{10}H_{21}$. Calculated in %: C 43.56; H 7.67; Cl 38.62. Found in %: C 43.68, 43.71; H 7.79, 7.71; Cl 38.21, 38.03.

The telomerization reaction studied by us, just as the addition reactions described in the literature, proceeded by rupture of the Si — H bond, as was substantiated by the absence of this bond in the compounds obtained. The structures of the alkyltrichlorosilanes were confirmed by molecular-refraction determinations and also by the preparation from them of the corresponding trimethylalkylsilanes by Grignard reaction. The properties of the trimethylalkylsilanes obtained are presented in Table 2.

TABLE 2

n	Formula*	B.p., °C/mm	n_D^{20}	d_4^{20}	*MR*		C in %		H in %		Si in %	
					calc.	found	calc.	found	calc.	found	calc.	found
2	$C_4H_9Si(CH_3)_3$	115	1.4035	0.7263	44.14	44.12	64.66	64.44 64.47	13.85	13.83 13.87	21.57	21.29 21.46
3	$C_6H_{13}Si(CH_3)_3$	163	1.4104	0.7412	53.35	53.58	68.30	68.48 68.28	14.01	14.02 14.02	17.73	17.56 17.61
4	$C_8H_{17}Si(CH_3)_3$	75/10	1.4232	0.7636	62.58	62.21	70.89	71.03 71.14	14.07	14.03 14.18	15.05	14.59 14.53

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* See [18] for literature data on the constants of these compounds.

The yields of alkyltrichlorosilanes of different molecular weight showed a certain regularity characteristic of telomerization reactions (also noted by us for the case of the telomerization of methyldichlorosilane with ethylene): the maximum yield was obtained for the compound for which n = 2 (25-26%). The yields of the remaining alkyltrichlorosilanes decreased with an increase in the value of n, comprising 4% of the total products for n = 5.

SUMMARY

The thermal telomerization of trichlorosilane with ethylene was carried out at a temperature of 270-285° and a pressure of 200 atm. Of the mixture of products obtained, alkyltrichlorosilanes of the structure $Cl_3Si(CH_2CH_2)_nH$, where n = 1 - 5, were individually isolated, and their trimethyl derivatives were prepared by Grignard reaction.

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ON SULFIDES OF LANTHANUM

N. P. Zvereva

(Presented by Academician I. I. Chernyaev, October 12, 1956)

Only one sulfide of lanthanum, La_2S_3, is known (not counting LaS_2, which dissociates at 680° with the formation of La_2S_3), and the data on it are contradictory. Thus, melting points from 2100-2150° [1, 3] to 2750° [2] have been given for it, and its outward appearance has been described both as a black vitreous mass [4] and as hexagonal plates of a light yellow or orange color [2].

By analogy to the cesium sulfides [5, 6], it was assumed that, in addition to lanthanum sesquisulfide, lower sulfides also exist, particularly the monosulfide LaS which should be higher melting than La_2S_3, and could be interesting as a highly refractory material. We prepared this compound, and investigated some of its properties.

The starting materials were lanthanum nitrate and metallic lanthanum of the following chemical composition: $La(NO_3)_3$: La_2O_3 in $\Sigma R_2O_3 > 99.5\%$, traces of Fe, traces of Si; La: $R_2O_3 = 99.8\%$, in which La = 99.7%, Fe = 0.01%, and Si ~ 0.05%.

20 g of free-flowing lanthanum nitrate powder was chlorinated in quartz ampoules with CCl_4 vapor, which was passed through the powder at a rate of about 50 cc/hour at 800 ± 5° for 3 hours. The CCl_4 was predried with phosphorus pentoxide, and was subsequently triple-distilled.

The chlorination product – a white, unsintered, crystalline powder with a particle size to 0.5 mm – dissolved in water without leaving a residue and, by analysis, contained 43.2% Cl (theoretical chlorine content of $LaCl_3$ is 43.4%, which indicated complete chlorination. Owing to the extremely great hygroscopicity of the chloride, all manipulations with it were carried out in an air-tight chamber in an atmosphere of dry argon.

The lanthanum trichloride was sulfided in the same quartz ampoule at 800° in a stream of hydrogen sulfide. The time for 20 g was 3 hours; the H_2S rate was 4 liters/hour.

Traces of moisture in the hydrogen sulfide were frozen out in a trap cooled with solid carbon dioxide or a mixture of benzene and liquid nitrogen at the temperature of incipient condensation of H_2S (− 63 to − 65°).

The sulfided product – unsintered, crystalline powder with a vermillion color and a particle size to 0.5 mm – contained, by chemical analysis, 25.4% S (theory required 25.5%), which corresponds to the formula La_2S_3. As do other rare earth sulfides, La_2S_3 undergoes hydrolysis in the presence of moisture. Therefore, all subsequent operations with it were carried out in a special "dry" chamber in an atmosphere of argon which had been dried by passage through a trap cooled with liquid nitrogen.

Calcination of tablets of La_2S_3 at 1700-1800° under a vacuum of $10^{-4}-10^{-5}$ mm Hg led to a change in its original color to dark gray. (Tablets with a weight of ~1 g, which were pressed from pulverized La_2S_3 which had been passed through a 74 μ mesh sieve, were placed in tantalum beakers with covers, and rapidly transferred from the "dry" chamber to the furnace.) The loss in weight on calcination was ~0.8%, shrinkage ~ 3.3%. With rapid cooling, cracks were formed on the samples, which indicated poor thermal strength of the material. Chemical analysis of the gray product showed a lower sulfur content than in the original red La_2S_3 – a total of 22.37%, which, by analogy to cesium sulfides, apparently corresponded to the solid solution La_2S_3-La_3S_4.

On heating in the same furnace at 2000° for 40 minutes, the La_2S_3 tablets melted and vaporized, and there was formed on the beaker covers a small amount of condensate, lustrous black crystals. X-ray analysis gave a powder spectrogram with well-defined, sharp lines belonging to a hexagonal structure of the type of cesium oxysulfide [6].

Thus, partial vaporization and decomposition of La_2S_3 occurs during heating in a high vacuum at temperatures to 1800°. This forms a new sulfide of the composition La_2S_3-La_3S_4 which melts in the range 1800-2000° and volatilizes readily, the vapor of which is oxidized by the residual oxygen in a vacuum to the nonvolatile and higher melting $La_2O_2S_3$.

LaS was prepared by reduction of La_2S_3 with metallic lanthanum by the "impregnation" method. For this purpose, porous crucibles having a volume of 0.5 cc were prepared from La_2S_3 by pressing under a pressure of 1 ton/cm^2 and firing in a vacuum of 10^{-4} - 10^{-5} mm Hg at a temperature of 1800° for 10 minutes, and subsequently cooling slowly. Metallic lanthanum, previously purified from surface oxide film, was charged to the crucibles in amounts somewhat exceeding stoichiometric, and the crucibles were then placed in the vacuum furnace. The action of the liquid metal, which permeated the crucible pores by capillary action, began at 1250°, but proceeded very slowly. Good results were obtained at 1600° with a holding time of 10 minutes.

The reaction product was a golden-yellow substance with a sulfur content of 19.7% (theoretical sulfur content of LaS is 18.75%).

X-ray powder spectrograms with lines belonging to only one cubic phase showed that this substance, isostructural to CeS, crystallized with an NaCl-type lattice with an identity period of 5.83 ± 0.01 kX, which gave a calculated density of 5.36 g/cc. Thus, this substance was identified as lanthanum monosulfide, LaS.

The microstructure of this LaS was two-phase: coarse, oval, yellow grains of LaS at the boundaries of which was distributed a light gray phase of lanthanum oxysulfide (judging from the weak etching in CH_3COOH). Estimation of the surfaces occupied by the two phases showed that the monosulfide had the composition: LaS, 95-97%; oxysulfide, ~3-5%. The microhardness of the LaS (yellow grains) by the Vickers method with a 20 g load was 197 ± 1.5 kg/mm^2, which indicates its metallic character. Pieces of LaS did not melt when heated under vacuum to 2100°.

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ON THE VALUES OF BOND ENERGIES OF NICKEL CATALYSTS WITH ELEMENTS OF ORGANIC COMPOUNDS

S. L. Kiperman and Academician A. A. Balandin

In solving the problem of the scientific selection of catalysts, the determination of the energies of the bonds of the catalyst with various elements is of substantial importance. Of the catalysts which can be used for this purpose, we make reference to thermochemical, chemisorption [1], and kinetic [2] methods. The kinetic method has previously been used only for oxide catalysts [3, 4]. Below, we present an attempt to use this method for the calculation of the bond energies of nickel catalysts with elements of organic compounds, with the aid of reactions which have not previously been used.

The bond energy of nickel catalyst with hydrogen, Q_{H-Ni}, and deuterium, Q_{D-Ni}. We will use ortho-para-hydrogen conversion (1) and isotopic exchange of hydrogen and deuterium (2), which were studied by Fajans [5] under equivalent conditions at 36-100° C on nickel plate activated by alternate oxidation and reduction. The mechanisms of these reactions are still under discussion [6]. Assuming that the indicated reactions are limited by the interaction on the catalyst surface of adsorbed components (adsorption stage), we represent both reactions by the doublet scheme of the multiplet theory [7], and write the expressions for the heights of the energy barriers, E, of the reactions [2]:

$$-2Q_{H-H}^{para} + 4Q_{H-Ni} = E_1. \tag{1}$$

$$-Q_{H-H} - Q_{D-D} + 2Q_{H-Ni} + 2Q_{D-Ni} = E_2. \tag{2}$$

(Q_{H-H}^{para}, Q_{D-D} and Q_{H-H} are the corresponding energies required to rupture the bonds in the molecules.)

Hence, taking into account the ratio $\varepsilon = -(^3/_4)E$ [2], we have:

$$Q_{H-Ni} = {}^1/_2 Q_{H-H}^{para} - {}^1/_3 \varepsilon_1. \tag{3}$$

$$Q_{D-Ni} = {}^1/_2 (Q_{D-D} + Q_{H-H} - Q_{H-H}^{para}) - {}^1/_3 (2\varepsilon_2 - \varepsilon_1), \tag{4}$$

where ε_1 and ε_2 are, respectively, the activation energies for Reactions (1) and (2). Substituting $Q_{H-H} = 104.2$ kcal [8], $Q_{D-D} = 105.96$ kcal [9] (the difference of Q_{H-H} for ordinary hydrogen at 298.1° K and Q_{H-H}^{para} is insignificant [12]), $\varepsilon_1 = 5910$ cal/mole, and $\varepsilon_2 = 7290$ cal/mole [5], we obtain $Q_{H-Ni} = 50.1$ kcal and $Q_{D-Ni} = 50.1$ kcal. According to an evaluation from thermochemical data [10], $Q_{H-Ni} = 55$ kcal; Eley, using Pauling's equation, estimated $Q_{H-Ni} = 60.2$ kcal [11].

Using the values $\varepsilon_1 = 7600$ cal/mole and $\varepsilon_2 = 9500$ cal/mole, which were obtained after a decrease in catalyst activity [5], we arrive at $Q_{H-Ni} = 49.6$ kcal and $Q_{D-Ni} = 49.5$ kcal; i.e., a change in the activity of the catalyst has only a small effect on Q_{H-Ni} and Q_{D-Ni}.

If the reactions under consideration are limited by the desorption stage (the mechanism of Bonhoeffer and Farkas [16]), then from the expressions for the second stage process [2] we obtain $Q_{H-Ni} = 51.1$ kcal and $Q_{D-Ni} = 50.9$ kcal.

We shall now use these values of Q_{H-Ni} and Q_{D-Ni} for approximate calculations of the energies of the bonds of nickel catalysts with other elements using other reactions in which hydrogen is activated, assuming that the transition to other forms of nickel does not introduce appreciable changes in Q_{H-Ni} and Q_{D-Ni}.

The bond energy of nickel catalyst with carbon at a double bond $Q_{=C-Ni}$. We use the data of Twigg [13] on the hydrogenation of ethylene at 70-100° C over nickel wire activated by alternate oxidation and reduction. Here:

$$Q_{=C-Ni} = {}^1/_2(Q_{C=C} + Q_{H-H}) - Q_{H-Ni} - {}^2/_3\varepsilon_3, \tag{5}$$

where ε_3 is the activation energy and $Q_{C=C}$ is the energy for rupture of one of the bonds of C = C. Substituting $\varepsilon_3 = 8200$ cal/mole [13], $Q_{C=C} = 46.7$ kcal, $Q_{H-H} = 104.2$ kcal [8], and $Q_{H-Ni} = 50.1$ kcal, we obtain $Q_{=C-Ni} = 19.9$ kcal. According to an estimate based on the ease with which various organic reactions take place [10], $Q_{=C-Ni} = 13$ kcal.

For this same reaction at 20-160° C over nickel film, according to the data of Jenkins and Rideal [14], $\varepsilon_3 = 10200$ cal/mole, whence, $Q_{=C-Ni} = 18.6$ kcal, i.e., there is little change in $Q_{=C-Ni}$ with the transition to another form of nickel.

For the isotope exchange $C_2H_4 + D_2$ [13] under the same conditions as in [14], the activation energy $\varepsilon_4 = 17200$ cal/mole. In this case, we have:

$$Q_{=C-Ni} = Q_{D-D} + Q_{C-H} - 2Q_{D-Ni} - Q_{H-Ni} - {}^4/_3\varepsilon_4, \tag{6}$$

where Q_{C-H} is the energy to rupture the C – H bond and is equal to 90.5 kcal [8]. Substituting $Q_{H-Ni} = Q_{D-Ni} = 50.1$ kcal and the other values given above, we obtain $Q_{=C-Ni} = 23.2$ kcal. Eley [11], by means already mentioned, obtained for the adsorption (and not for the reaction) the considerably higher value $Q_{=C-Ni} = 50.6$ kcal.

Bond energy of nickel catalyst with carbon Q_{C-Ni} (with a single bond at the carbon). This value can be calculated from the data of Morikawa, Benedict and Taylor [15] on the hydrogenolysis of ethane $C_2H_6 + H_2 = 2CH_4$ in the interval 100-130° C over nickel catalyst supported on kieselguhr. For this reaction

$$Q_{C-Ni} = {}^1/_2(Q_{C-C} + Q_{H-H}) - Q_{H-Ni} - {}^2/_3\varepsilon_5, \tag{7}$$

where the activation energy $\varepsilon_5 = 43000$ cal/mole [15]. Substituting $Q_{C-C} = 66.3$ kcal [8], $Q_{H-Ni} = 50.1$ kcal, and the remaining values as given above, we obtain $Q_{C-Ni} = 6.5$ kcal. According to one estimate [10], $Q_{C-Ni} = 6$ kcal.

For the isotope exchange $CH_4 + D_2$, which was studied in [15], at 110-184° C:

$$Q_{C-Ni} = Q_{C-H} + Q_{D-D} - Q_{H-Ni} - 2Q_{D-Ni} - {}^4/_3\varepsilon_6, \tag{8}$$

Substituting the activation energy $\varepsilon_6 = 28000$ cal/mole [15], $Q_{H-Ni} = Q_{D-Ni} = 50.1$ kcal, and other values given above, we obtain $Q_{C-Ni} = 8.9$ kcal. Average $Q_{C-Ni} = 7.7$ kcal.

For this same isotope exchange reaction over a more active catalyst—nickel films—and at higher temperatures (206-2[illegible]°C), according to the data of [22], ε_6 = 23800 cal/mole; whence Q_{C-Ni} = 14.5 kcal.

Bond energy of nickel catalyst with oxygen Q_{O-Ni}. We use the data of van Mechelen and Jungers [18], who studied the hydrogenation of acetone in an autoclave at temperatures of 108-150°C over skeletal nickel. The activation energy is ε_7 = 9500 cal/mole (for other aliphatic ketones, approximately the same values were obtained). For this reaction:

$$Q_{O-Ni} = Q_{C-O} + Q_{H-H} - Q_{C-Ni} - 2Q_{H-Ni} - {}^4/_3\varepsilon_7 \qquad (9)$$

(Q_{C-O} is the energy to rupture one of the C–O bonds, and is equal to 83.4 kcal [8].) Substituting Q_{C-Ni} = [illegible] kcal, Q_{H-Ni} = 50.1 kcal, and other values given above, we obtain Q_{O-Ni} = 54.8 kcal. According to one estimate [10], Q_{O-Ni} = 48.5 kcal. Thermochemically, Q_{O-Ni} = 59 kcal [10].

For the isotope exchange reaction $CH_3OH + D_2 = CH_3OD + HD$, we have

$$Q_{O-Ni} = Q_{O-H} + Q_{D-D} - Q_{H-Ni} - 2Q_{D-Ni} - {}^4/_3\varepsilon_8. \qquad (10)$$

(Q_{O-H} is the energy to rupture the O–H bond, and is equal to 110.6 kcal [8].) Substituting the activation energy ε_8 = 6600 cal/mole [19] for nickel films in the interval 0-41.5°C, Q_{H-Ni} = 50.1 kcal, Q_{D-Ni} = 50.1 kcal, and the remaining values given above, we obtain Q_{O-Ni} = 57.5 kcal. During a study of the chemisorption equilibrium of oxygen on nickel catalyst by the method of reference [1], we obtained for average coverage of the surface by oxygen the value Q_{O-Ni} = 56.1 kcal.

Bond energy of nickel catalyst with nitrogen, Q_{N-Ni}. We use the ammonia-deuterium isotope exchange reaction, which has been studied over nickel films. For this reaction:

$$Q_{N-Ni} = Q_{N-H} + Q_{D-D} - Q_{H-Ni} - 2Q_{D-Ni} - {}^4/_3\varepsilon_9, \qquad (11)$$

where Q_{N-H} is the energy to rupture the N–H bond, equal to 84.3 kcal [8], and ε_9 is the activation energy. In various works, depending on the activity of the film, the value of ε_9 varies from 8700-9300 cal/mole [20] to 14700-16100 cal/mole [21]. Over the least active films, the value of ε_9, although obtained in the interval 200-300°C, corresponded, as indicated by the authors [21], to the activity in the initial experiments at room temperature. Substituting in Equation (11) ε_9 = 16100 cal/mole for the least active films [21], Q_{H-Ni} = 50.1 kcal, Q_{D-Ni} = 50.1 kcal, and the other values given above, we obtain Q_{N-Ni} = 18.6 kcal. According to one estimate [10] (from a comparison of the ease with which the reactions occur) Q_{N-Ni} = 18 kcal. A change in the activity of this same catalyst (ε_9 = 14700 cal/mole [21]) leads to Q_{N-Ni} = 20.4 kcal. For the more active films (ε_9 = 9300 – 8700 cal/mole [20]), we obtain Q_{N-Ni} = 27.6-28.4 kcal.

As seen from the data presented, the kinetic method can be used for the determination of the bond energies of nickel catalysts with different elements using such reactions as ortho-para-hydrogen conversion, isotope exchange, hydrogenation, and hydrogenolysis. These values are in general agreement with those calculated by a completely different method [10]. The bond energy Q_{D-Ni} is practically no different from Q_{H-Ni} (the difference between the zero point energies for Ni–H and Ni–D, 0.7 kcal [17], is within the limits of sensitivity of the method).

A variation in the activity of the catalyst leading to a change in ε of several thousand cal/mole has little effect on the value of Q, and, in a number of cases, had little effect in the change to another form of catalyst; however, a two-fold change in ε_9 leads to a change in Q_{N-Ni} of 50%. In almost all cases, Q for films is higher than for other catalyst forms.

It is important that, using different reactions for the calculation of the same Q, we obtain approximately the same, and sometimes coinciding, values. To a first approximation, the method can be used for the calculation of bond energies for different forms of the catalyst.

In some cases, the values obtained are lower than those obtained from thermochemical data (cf. [2, 10]). This indicates that the surface compounds are less stable than the corresponding compounds in the bulk.

Using the bond energies calculated above for the calculation of the adsorption potential q (i.e., the sum of the bond energies of the reacting atoms with the catalyst) for the dehydrogenation of formic acid over Ni:

$$q = Q_{=C-Ni} + Q_{O-Ni} + 2Q_{H-Ni}; \tag{12}$$

substituting $Q_{=C-Ni} = 19.9$ kcal, $Q_{H-Ni} = 50.1$ kcal, $Q_{O-Ni} = 54.8$ kcal, we obtain $q = 174.9$ kcal. On the other hand, we have:

$$q = Q_{C-H} + Q_{O-H} - {}^4/_3\,\varepsilon_{10}, \tag{13}$$

where ε_{10} is the energy of activation. Noting from tables that $Q_{C-H} = 90.5$ kcal and $Q_{O-H} = 110.6$ kcal [8] and taking the experimental value of $\varepsilon_{10} = 19700$ cal/mole, according to the data of Toyama and Kubokawa [23] who worked at 143-160°C, we can calculate q by Equation (13); this gives $q = 174.8$ kcal, in excellent agreement with the value found above by an independent route.

In the present work, the following values of Q (in kcal) were obtained for the first stage reaction mechanism proceeding over nickel wires, plate, low activity films, or porous catalysts: $Q_{H-Ni} = 50.1$; $Q_{D-Ni} = 50.1$; $Q_{=C-Ni} = 19.9$; $Q_{C-Ni} = 7.7$, $Q_{O-Ni} = 54.8$; $Q_{N-Ni} = 18.6$.

In conclusion, we calculated from these values of Q the values of the adsorption potentials, q, and also the energy barriers, E, using also the heats of reaction, u, and the sums of the energies of formation and rupture of the bonds, s, from the relation $q - s/2 + u/2 = E$ [2] (Table 1).

TABLE 1

Adsorption Potentials, q, and Energy Barriers, E, over Ni (in kcal)

Reaction	$u/2$	$s/2$	q	$-E$
I. $p\text{-}H_2 \rightarrow o\text{-}H_2$	0	208.4	200.4	8.0
II. $H_2 + D_2 \rightarrow 2HD$	0	210.2	200.4	9.8
III. $C_2H_4 + H_2 = C_2H_6$	15.0	165.9	140.0	10.9
IV. $CH_3OH + D_2 = CH_3OD + HD$	0	216.6	205.1	11.5
V. $CH_3COCH_3 + H_2 = CH_3CH(OH)CH_3$	6.8	194.4	174.9	12.7
VI. $NH_3 + D_2 = NH_2D + HD$	0	190.3	168.9	21.4
VII. $C_2H_4 + D_2 = C_2H_3D + HD$	0	196.5	170.2	26.3
VIII. $HCOOH = H_2 + CO_2$	−6.8	194.4	174.9	26.3
IX. $CH_4 + D_2 = CH_3D + HD$	0	196.5	158.0	38.5
X. $C_2H_6 + H_2 = 2CH_4$	5.3	175.7	115.6	54.8

It is seen that for the majority of these reactions over nickel catalyst, q approximates s/2, i.e., optimum. Reaction X is the most difficult to carry out.

It is noteworthy that the use of the kinetic method of determining bond energies in simple reactions proceeding over metallic nickel gives results which are close to those calculated from thermochemical data and from a comparison of the ease with which reactions of more complex organic compounds proceed.

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A NEW ROUTE FOR THE PREPARATION OF TROPYLIUM AND METHYLTROPYLIUM COMPOUNDS

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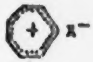
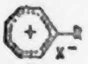
Up to the present time, two routes, differing in principle, have been known for the formation of the seven-membered aromatic system tropylium (I).



I



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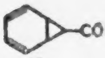
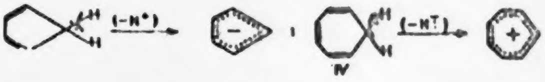


III

Doering and Knox [1] first obtained tropylium bromide (I, X = Br) by splitting out HBr from dibromocycloheptadiene. It was next established [2] that salts of carboxytropylium (II, R = COOH) could be prepared by this same method, although in very small yield (0.8%). The other method, which was developed by Dewar and Pettit [3], was based on the easy isomerization of the norcaradiene system to the tropylium system. Thus, tropylium isocyanate was obtained by Curtius rearrangement of the azide of norcaradienecarboxylic acid (III), and the salt of methyltropylium (II, R = CH_3) was obtained from the azide of methylnorcaradienecarboxylic acid.

Therefore, it was certainly of interest to substantiate the possibility of the direct transition from the cycloheptatriene (tropylidene) system (IV), with three double bonds, to the aromatic tropylium system. By splitting off somehow a hydrogen atom with its pair of electrons from a CH_2 group with the resulting transition of the seventh carbon atom from the state of sp^3 hybridization to a state of sp^2 hybridization, cyclic conjugation of all six π-electrons of the double bonds should be possible, leading to the formation of the aromatic tropylium system. Such a transition should be similar in nature to the corresponding transition of cyclopentadiene to cyclopentadienyl anion under the influence of alkali metals and strong bases. However, in contrast to cyclopentadiene, where a proton is removed, a hydrogen with its pair of electrons (hydride ion) must be removed from cycloheptatriene:



In both cases, a nonbenzenoid aromatic system with 6 π electrons is formed.

In searching for a route for such a direct conversion of cycloheptatriene to tropylium salts, we studied the action on cycloheptatriene of a number of electrophilic reagents—strong acids, halogen derivatives, etc. Many of these substances reacted vigorously with the double bonds of cycloheptatriene, so that the reaction forming tropylium was hindered.

An exothermic reaction accompanied by tar formation resulted from the action of concentrated sulfuric acid on cycloheptatriene. However, in addition, oxidation of the tropylidene occurred with the formation of appreciable amounts of tropylium salts (18% yield):

$$C_7H_8 + 2H_2SO_4 \rightarrow C_7H_7^+ + HSO_4^- + 2H_2O + SO_2$$

The formation of an aromatic carbonium ion—tropylium—by the action of concentrated sulfuric acid on cycloheptatriene is similar to the formation of aliphatic carbonium ions by the action of concentrated H_2SO_4 on saturated hydrocarbons with a tertiary carbon atom. Such an analogy is indirect confirmation of the mechanism, assumed in the last case, of deuterium exchange and other reactions [4].

Just as in the case of saturated hydrocarbons, acids which do not possess oxidizing properties—concentrated phosphoric acid, hydrochloric acid—do not bring about the conversion of cycloheptatriene to tropylium either in the cold or on heating. Concentrated nitric acid reacts with cycloheptatriene very vigorously; in this case, the formation of small amounts of tropylium takes place.

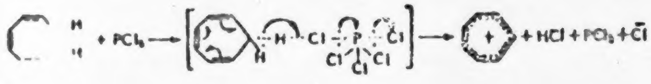
A study of the action of other oxidizing agents on cycloheptatriene confirmed that the latter is converted into tropylium to some degree or other by oxidation in acid medium. Thus, CrO_3 in glacial acetic acid converts cycloheptatriene to tropylium with a yield of up to 34%. About 7% of tropylium salts is formed by refluxing tropylidene with SeO_2 in aqueous dioxane in the presence of sulfuric acid.

Such strong electrophilic reagents as boron trifluoride and aluminum chloride should react with cycloheptatriene, converting it to tropylium according to:

$$C_7H_8 + BF_3 \dashrightarrow C_7H_7^+ + [HBF_3]^-$$

However, BF_3 and $AlCl_3$ react so vigorously with the double bonds that, although the reaction forming tropylium proceeds, it does so to a very slight extent. Heating tropylidene with boron trifluoride etherate forms about 2% tropylium salts along with a large amount of polymer. About 18% of tropylium salts were formed by the reaction of tropylidene with anhydrous aluminum chloride.

It would be expected that halogen compounds of elements with variable valence would be able to abstract a pair of electrons from cycloheptatriene, converting it to tropylium. Actually, it developed that phosphorus pentachloride reacts extremely readily with cycloheptatriene. This formed tropylium chloride, and the phosphorus pentachloride was reduced to the trichloride:



The reaction proceeded with practically quantitative yield at room temperature, and was not accompanied by tar formation or any other side reactions.

This reaction of cycloheptatriene with phosphorus pentachloride can serve as an excellent preparative method for the preparation of salts of tropylium and its derivatives. Advantages of this method are the high yield of tropylium, the mild conditions, and the simplicity with which the reaction is carried out. Increased yields of tropylium chloride are favored by an excess of PCl_3 and by carrying out the reaction without heating and in an inert solvent. The tropylium formed is best separated by converting it into the difficultly soluble perchlorate, chloroplatinate [5], or iodide, rather than as the unstable and very hygroscopic tropylium chloride.

The method developed was also used for the preparation of salts of methyltropylium (II, $R = CH_3$). The reaction of methylcycloheptatriene with phosphorus pentachloride proceeded very rapidly and smoothly in the cold. Methyltropylium chloride was obtained and converted into the difficultly soluble methyltropylium chloroplatinate. At the same time, an attempt to prepare methyltropylium salts by the method of Doering and Knox [1] led only to the formation of tars. The preparation by this method of other substituted tropyliums is being studied.

As would be expected, phosphorus trichloride, in contrast to the pentachloride, does not convert cycloheptatriene to tropylium. Nor does this reaction proceed with phosphorus tribromide. Phosphorus pentabromide readily dissociates under ordinary conditions; therefore, in its reaction with cycloheptatriene bromine is readily added without the formation of tropylium bromide.

The reaction of cycloheptatriene with sulfuryl chloride proceeds similarly to the reaction with phosphorus pentachloride:

$$C_7H_8 + SO_2Cl_2 \longrightarrow C_7H_7^+ + Cl^- + SO_2 + HCl$$

This reaction gives 25% tropylium salt; however, the reaction is accompanied by the formation of appreciable tar. Thionyl chloride does not react with cycloheptatriene.

Thus, it was shown that the action on cycloheptatriene of various electrophylic reagents (H_2SO_4, HNO_3, CrO_3, BF_3, $AlCl_3$, SeO_2, SO_2Cl_2, and PCl_5) splits a pair of electrons and an atom of hydrogen from the cycloheptatriene and converts it to the aromatic tropylium system. The reaction of cycloheptatriene (and its derivatives) with phosphorus pentachloride can serve as a method for the preparation of tropylium derivatives.

EXPERIMENTAL

The initial cycloheptatriene was prepared by the photochemical reaction of benzene with diazomethane [6]. After distillation in a column of 40 theoretical plates, a fraction was isolated boiling at 116.3-117.0°/744 mm, n_D^{19} 1.5228, containing 95% cycloheptatriene and 5% toluene.

Reaction with Sulfuric acid. 0.083 g of cycloheptatriene was added, with cooling and stirring, to 2 ml of concentrated sulfuric acid. The red solution stood for 10 days at room temperature, and was then carefully diluted twofold with water while cooling. Tropylium chloroplatinate was precipitated from the solution by the addition of chloroplatinic acid. The precipitate was filtered, washed with alcohol, and dried. The yield of tropylium chloroplatinate was 0.048 g (18% of theoretical).

In the experiments with CrO_3, BF_3, $AlCl_3$, HNO_3, SeO_2, and SO_2Cl_2, the tropylium salts formed were similarly isolated in the form of the chloroplatinate.

Reaction with Phosphorus pentachloride. In a flask fitted with a stirrer and reflux condenser, the latter being protected by a calcium chloride tube, was placed 4.1 g (~0.02 mole) of PCl_5 and 40 ml of CCl_4, and, while stirring, 0.91 g (0.0099 mole) of cycloheptatriene in 10 ml of CCl_4 was added. Immediately, a copious, white precipitate began to form. The reaction mixture was stirred about an hour, and was then refluxed for 15 minutes. After cooling, the reaction mixture was rapidly suction-filtered in a funnel, washed with CCl_4, and, with cooling, was treated with 4 ml of water (vigorous reaction). The reaction flask and the funnel were washed with a small amount of alcohol. The aqueous alcohol solution obtained (the CCl_4 layer on the bottom did not interfere with further operations) was treated with a slight excess of 30% $HClO_4$. Immediately, a copious precipitate of tropylium perchlorate formed, which, after cooling, was filtered and washed with cold alcohol. The perchlorate, without recrystallization, was sufficiently pure for further work. The yield of tropylium perchlorate was 1.49 g (80% of theoretical). Additional tropylium was precipitated in the form of the chloroplatinate by the addition of H_2PtCl_6 to the filtrate; yield, 0.30 g (10% of theoretical). The total yield of tropylium was 90%. When this same reaction was carried out without heating, but with 2.5-hour stirring and standing overnight, the tropylium yield reached 98%.

In special experiments carried out for the purpose of identification, the tropylium chloride formed in the reaction was isolated; it was a hygroscopic substance, readily soluble in water, which, after recrystallization from nitromethane, melted at 97°. According to the literature data [1], it melts at 102°. The aqueous solution gave a positive reaction for Cl^- (tested with $AgNO_3$) and for tropylium ion – formation of precipitates with $HClO_4$, H_2PtCl_6, and $NaB(C_6H_5)_4$ [6].

Found %: C 28.26, 28.38; H 2.61, 2.49; Pt 33.21, 32.98 $C_{14}H_{14}PtCl_6$. Calculated %: C 28.49; H 2.39; Pt 33.08.

Methylcycloheptatriene, the starting material for the preparation of methyltropylium, was synthesized by the photochemical reaction of toluene with diazomethane. Distillation in a column isolated a fraction (b.p. 138.2-139.0°/730 mm, n_D^{20} 1.5114) containing 70% methylcycloheptatriene. The reaction of methylcycloheptatriene with PCl_5 was carried out in a manner analogous to that described above. After a 1-hour standing at room temperature, the precipitate was filtered, and the methyltropylium formed was converted to the chloroplatinate – a yellow precipitate difficultly soluble in water and still more difficultly soluble in alcohol; it darkened at a temperature of ~140°. The yield was ~50%.

Found %: C 31.27; 31.22; H 3.20, 3.24; Pt 30.89, 30.75 $C_{16}H_{18}PtCl_6$. Calculated %: C 31.08; H 2.93; Pt 31.58.

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SYNTHESIS OF 4-ALKYL-1-AZADEHYDROQUINOLIZINIUM SALTS

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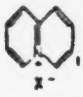
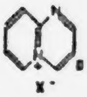
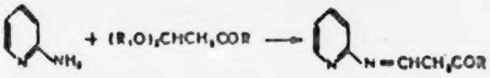
and N. K. Belsky*

In a series of works, published by us and N. K. Kochetkov and co-workers, the synthesis of a number of nitrogen and oxygen heterocyclic systems was carried out [1-10]. In this work, we started with β-chlorovinylketones or closely related derivatives. For some time past, the attention of investigators has been more and more attracted to the synthesis of condensed aromatic heterocyclic systems in which the hetero-atom is an ammonium nitrogen common to two rings, in particular, dehydroquinolizinium salts (I). In contrast to quinoline and isoquinoline, the chemistry of the dehydroquinolizinium ion [11-13] has been little studied. In the present work, we carried out the synthesis of a number of derivatives of a new condensed heterocyclic system, the aza analog of dehydroquinolizinium (II). 4-Alkyl-1-azadehydroquinolizinium salts were obtained by us from α-aminopyridine and β-ketoacetals. The latter were prepared in good yields from β-chlorovinylketones by the method developed by us together with N. K. Kochetkov [14].


I


II

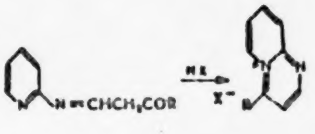
We found that β-ketoacetals enter into a condensation reaction with α-aminopyridine. In this work it was established that the acetal group enters into the reaction, since both the dimethyl acetal and the diethyl acetal of acetoacetaldehyde gave the same condensation product, namely 2-acetoacetalaminopyridine [2-N-(β-acetyl)ethylideneaminopyridine]:


where $R = CH_3^-$; $R_1 = CH_3^-$, $C_2H_5^-$

$R = C_2H_5^-$, C_3H_7, C_6H_5; $R_1 = CH_3^-$

The 2-acylacetalaminopyridine was a colorless or slightly colored material which was difficult to crystallize from various organic solvents.

Under the influence of concentrated acids the products of the condensation of α-aminopyridine with aliphatic β-ketoacetals cyclized with the elimination of water, forming a new heterocyclic system — 4 alkyl-1-azadehydroquinolizinium salts. The best results were obtained using perchloric and hydrobromic acids:


where $R = CH_3^-$, $C_2H_5^-$; $X = Br$, ClO_4.

$R = C_3H_7^-$; $X = ClO_4$

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* N. K. Belsky carried out the spectroscopic part of the work.

However, such cyclization did not occur where R = C_6H_5. In attempts to carry out this reaction with aqueous acid, acetophenone and a salt of α-aminopyridine were obtained, and α-aminopyridine hydrobromide and tribenzoylbenzene were obtained under the influence of gaseous hydrogen bromide in ether.

The 4-alkyl-1-azadehydroquinolizinium salts were crystalline substances, readily soluble in water, moderately so in hot alcohol, and insoluble in ether and benzene. The perchlorates were more stable than the bromides. The structure of these salts did not decolorize a dilute solution of potassium permanganate, and, consequently, did not have nonaromatic double bonds. 4-Methyl-1-azadehydroquinolizinium bromide was cleaved by the action of alkali with the formation of the original 2-acetylacetalaminopyridine. Apparently, substitution of the anion by the hydroxyl group occurs first, followed by cleavage of the ring. Thus, during cyclization of 2-acylacetalaminopyridines in acid medium, rearrangement does not occur, and, consequently, the alkyl substituent occupies the 4-position.

During catalytic hydrogenation over platinum, 4-methyl-1-azadehydroquinolizinium bromide absorbs five moles of hydrogen, which indicates the presence of five double bonds in the two condensed rings. 4-Methyl-1-azaoctahydroquinolizine hydrobromide was formed in the hydrogenation.

Absorption spectra in the ultraviolet region were taken of aqueous solutions of the salts (Fig. 1). The absorption curve of the 1-azadehydroquinolizinium ion was very characteristic and had six maxima (λ_{max}), which agreed for all of the salts used: 336, 318, 312, 304, 274, and 228 mμ (Fig. 1). From the spectral data, it is seen that the character of the spectrum is determined by the azadehydroquinolizinium nucleus.

The region of absorption and the character of the spectrum of this nucleus is very similar to the region and character of the absorption of quinoline and isoquinoline, which also serves as confirmation of the structure proposed by us. Of course, the second nitrogen atom introduces some difference. The absorption spectrum of the azadehydroquinolizinium nucleus, just as the absorption spectra of quinoline [15] and isoquinoline [16], is divided into three parts: 1) in the region of 350-290 mμ there are several narrow and sharp absorption bands; 2) a broad band at a wave length of λ = 282 mμ; 3) a broad and intense band at a wave length of 228 mμ. The distribution of intensities among bands is also similar. For all of these compounds, the intensities of the group of bands at 350-290 mμ and 282 mμ differed little from each other, the short wavelength band at 228 mμ is far more intense than all of the others.

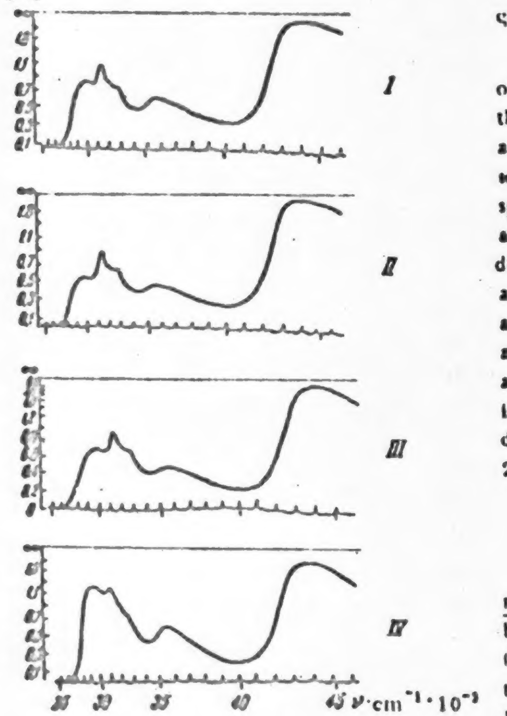


Fig. 1

EXPERIMENTAL

2-Acylacetalaminopyridines [2-N-(β-acyl)ethylideneaminopyridines]. The 2-acylacetalaminopyridines were prepared by heating a mixture of 0.11 mole of α-aminopyridine and 0.1 mole of the appropriate β-ketoacetal in sealed ampules to 140° for 5-6 hours. After opening the ampules, the crystallized reaction product was removed to a porous filter, and washed several times with ether. The 2-acylacetalaminopyridines were recrystallized from acetone or a mixture of alcohol and petroleum ether (Table 2).

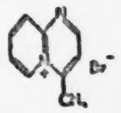
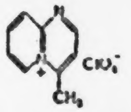
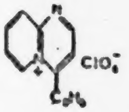
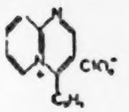
4-Methyl-1-azadehydroquinolizinium bromide. 1 g of 2-acetoacetalaminopyridine was dissolved in 1.2 ml of concentrated hydrobromic acid. To the solution was added alcohol and then ether until a precipitate formed. The precipitate was filtered rapidly, and washed with a mixture of absolute alcohol and ether (1 : 10) and then with absolute ether. The yield was 1.1 g (75.8% of theoretical). It decomposed at 204-205° (began to darken at 170°) after recrystallization from alcohol, Found %: C 47.82; 47.94; H 4.06; 4.11; N 12.29; Br 35.65 $C_9H_9N_2Br$. Calculated %: C 48.01; H 4.02; N 12.44; Br 35.55

4-Methyl-1-azadehydroquinolizinium perchlorate. A mixture of 1.8 g of 2-acetoacetalaminopyridine and 2 ml of 70% perchloric acid was heated on a water bath until the precipitate completely dissolved, and then 3 ml of absolute alcohol was added. The precipitated colorless crystals were filtered and washed on the filter with absolute alcohol. The yield was 1.4 g (77.8% of theoretical). The colorless crystals were lamellar. They decomposed at 225° (began to darken at ~200°) after recrystallization from 50% methanol.

Found %: C 44.14; 44.17; H 3.58; 3.63; N 11.52; 11.63; Cl 14.58; 14.32 $C_9H_9O_4N_2Cl$. Calculated %: C 44.26; H 3.71; N 11.46; Cl 14.48.

4-Ethyl-1-azadehydroquinolizinium bromide. To 1.3 g of 2-propionylacetalaminopyridine was added 2 ml of concentrated hydrobromic acid and then 1 ml of alcohol and 25-30 ml of ether. The yield was 1.1 g (64.0% of theoretical). After recrystallization from a mixture of alcohol and ether, the cream-colored crystals melted at 210-212°.

TABLE 1

№	4-Alkyl-1-azadehydroquinolizinium salt	Intensity $\varepsilon \cdot 10^{-4}$
I		0.7; 0.93; 0.72; 0.82; 0.5; 2.1
II		0.6; 1.0; 0.7; 0.09; 0.5; 0.48; 2.1
III		0.8; 1.1; 0.6; 0.77 0.66; 2.1
IV		1.3; 1.2; 0.9; 0.8; 0.6; 1.8

Found %: C 49.98; 50.16; H 4.60; 4.60 $C_{10}H_{11}N_2Br$. Calculated %: C 50.20; H 4.60

4-Ethyl-1-azadehydroquinolizinium perchlorate. To 1 g of 2-propionylacetalaminopyridine was added 1 ml of 70% perchloric acid and then 1 ml of absolute alcohol and 10 ml of ether. 1.09 g (74% of theoretical) of 4-ethyl-1-azadehydroquinolizinium perchlorate was obtained. After recrystallization from methanol, the colorless lamellar crystals melted at 169-170°.

Found %: C 46.60; 46.42; H 4.33, 4.25; N 10.81, 10.86; Cl 13.78, 13.65. $C_{10}H_{11}O_4N_2Cl$. Calculated %: C 46.42; H 4.28; N 10.83; Cl 13.73.

4-n-Propy-1-azadehydroquinolizinium perchlorate. To a solution of 1 g of 2-n-butyroacetalaminopyridine in 1.5 ml of 70% perchloric acid was added 10 ml of absolute alcohol, and then absolute ether was added until precipitation was complete. The yield was 0.95 g (64.2% of theoretical), m.p. 145°.

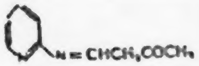
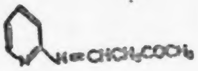
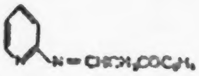
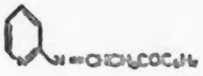
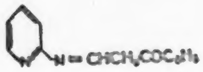
Found %: C 48.67; 48.41; H 4.79; 4.75; N 10.21; 10.04; Cl 12.71; 12.61 $C_{11}H_{13}O_4N_2Cl$. Calculated %: C 48.57; H 4.77; N 10.23; Cl 13.02

The action of alkali on 4-methyl-1-azadehydroquinolizinium perchlorate. To an aqueous solution of 2.3 g of 4-methyl-1-azadehydroquinolizinium perchlorate was added 0.4 g NaOH in 7 ml water, and the entire mass was extracted several times with benzene. The benzene extract was washed with water, and dried over sodium sulfate. The benzene was evaporated under vacuum; the crystalline residue (yield 1.4 g) had a m.p. of 117°. A mixture of a sample with 2-acetoacetalaminopyridine melted without depression of the melting point.

Hydrogenation of 4-methyl-1-azadehydroquinolizinium bromide. 1 g of 4-methyl-1-azadehydroquinolizinium bromide in solution in 150 ml of alcohol was hydrogenated in the presence of platinum black (300 mg) at room temperature and atmospheric pressure. Five moles of hydrogen was absorbed. The 4-methyl-1-azaoctahydroquinolizine hydrobromide obtained was difficult to purify; therefore, it was identified as the picrate, m.p. 112° (from alcohol).

Found %: N 18.15; 18.18 $C_{16}H_{21}O_7N_5$. Calculated %: N 18.19

TABLE 2

β-ketoacetal	2-Acylacetalaminopyridine	M.p., °C	Yield %	Analytical data found %	Analytical data calc., %
$CH_3COCH_2CH(OCH_3)_2$		121	61.8	C 66.66; 66.43 H 6.27; 6.21 N 17.40; 17.16	C 66.60 H 6.17 N 17.28
$CH_3COCH_2CH(OC_2H_5)_2$		121	49.4	—	—
$C_2H_5COCH_2CH(OCH_3)_2$		86.5–87	55.1	C 67.80 H 6.71 N 15.80	C 68.18 H 6.81 N 15.88
$n-C_3H_7COCH_2CH(OCH_3)_2$ B.p. 81°/10 mm n_D^{20} 1.4205		88–89	66.7	C 69.49; 69.22 H 7.38; 7.40 N 14.62; 14.78	C 69.47 H 7.37 N 14.73
$C_6H_5COCH_2CH(OCH_3)_2$ B.p. 134–135°/10 mm n_D^{20} 1.5385		127–128	53.6	C 75.07; 74.82 H 5.43; 5.41 N 12.45; 12.47	C 74.97 H 5.34 N 12.50

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ON THE NONCOPLANARITY OF BENZENE RINGS IN DERIVATIVES OF BIPHENYL

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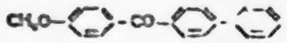
and S. G. Bogomolov

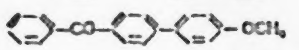
(Presented by Academician I. N. Nazarov October 16, 1956)

It has been established that the benzene rings in the biphenyl molecule in the crystalline state lie in one plane in spite of partial overlap of the spheres of the hydrogen atoms (in the ortho positions) [1]. Evidently, coplanarity of crystalline biphenyl depends on special conditions of packing of the molecules in the crystal, the energy involved in the small compression of the spheres of the hydrogen atoms being offset by the advantage of planar configuration [2]. At the same time, it is known that the phenyl groups are noncoplanar in liquid and gaseous biphenyl [3, 4]. Noncoplanarity of the rings in biphenyl in the absence of substituents in the ortho positions has also been shown for a number of p,p'-substituted biphenyls in solution [5-8]. Data on the structure of such derivatives in the crystalline state is, however, still lacking.

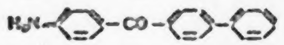
One of the possible routes for studying this question is spectroscopic investigation in the infrared region of crystals of compounds of biphenyl. In the present work, this method was used for the study of biphenyl ketones of the following structures:



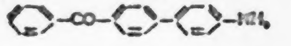
(I)



(II)



(III)



(IV)

In biphenyl p-anisyl ketone (I) and biphenyl p-aminophenyl ketone (III), the electron donor effect of the methoxy and amino groups is transmitted to the ketone group through the benzene rings, while in both p-methoxybiphenyl phenyl ketone (II) and p-aminobiphenyl phenyl ketone (IV), this effect is transmitted through the biphenyl system.

It might be expected that if the benzene rings in biphenyl are not coplanar, the mutual effect of the methoxy and amino groups with the carbonyl group in Compounds II and IV, owing to disruption of conjugation, will be less than in Compounds I and III. In order to confirm this, it was necessary to characterize the changes which occur due to the effects of these groups on the carbonyl during transmission of the effect through the phenyl and biphenyl systems. For this purpose we used the determination of the frequency of the valence vibrations of the carbonyl group in the infrared spectrum.

As is well known, the frequency of the valence vibration of the carbonyl group shifts in the long wavelength direction with an increase in the π-electron interaction of the carbonyl group with other electron donor groups in the molecule [9-13]. In conformity with this, the frequency of the vibration of the carbonyl group in Compound I must be lower than in Compound II and less in Compound II than in Compound IV if the rings are not coplanar.

An investigation of the ketones in dioxane solution was carried out simultaneously with the spectroscopic investigation of them in the crystalline state.

Polarography was also used for the investigation of the solutions. It is known that during reduction of ketones at the dropping mercury electrode, the half-wave potential ($\varphi_{1/2}$) becomes more negative with an increase in π-electron conjugation, i.e., with an increase in the effect of the electron donor group on the C=O group and an increase in the electron density at the latter [14]. From this it follows that in Compounds II and IV, in the event of noncoplanarity of the rings of the biphenyl radical when conjugation will be less, $\varphi_{1/2}$ will be more positive than in Compounds I and III. In the event of coplanarity, the values must be equal or must change in the opposite direction.

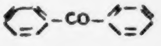
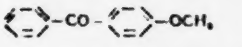
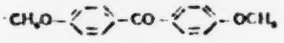
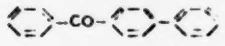
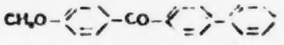
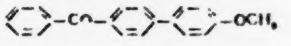
Besides the indicated biphenyl ketones (I-IV), the corresponding benzophenones were used in the investigation for purposes of comparison (see Tables 1 and 2). The spectra were taken on an IKS-11 infrared spectrometer in the 5-14 μ region with an NaCl prism and, for the amines, also in the 2-5 μ region with an LiF prism.

The materials were used in the crystalline state (in the form of a suspension in fluorinated hydrocarbon) and in solution in dioxane. The accuracy of the determination of the vibration frequency of the carbonyl group was ± 2-3 cm^{-1}.

The polarographic investigation was carried out with a Heyrovsky micropolarograph and with an ammoniacal buffer (pH 8.2). The accuracy of the determinations was ± 0.005 v.

All compounds were synthesized by literature methods, and were recrystallized to constant melting points.

TABLE 1

Compound	ν C=O, cm^{-1}		$\varphi_{1/2}$ with respect to nor. cal. elec. (in ammoniacal buffer, pH 8.4)
	crystals in polyfluoro-hydrocarbon	solution in dioxane	
	1661	1664	−1.360
	1647	1653	−1.420
	1642	1647	−1.605
	1653	1660	−1.275
	1642	*	−1.340
	1656	*	−1.275

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* Products insoluble in dioxane.

The results obtained are presented in Tables 1 and 2. For illustration, curves of parts of the infrared spectra of the methoxy compounds (Fig. 1) and the polarograms of the amino compounds (Fig. 2) are given.

As seen from the data of Table 1, the effect of the electron donor $-OCH_3-$ group was a decrease in the characteristic vibration frequency of the C=O group. The same effect was shown by the NH_2 group (Table 2).

In Compounds II and IV, where these groups act through the biphenyl system, this effect was practically unobserved, and the value of νC=O in these compounds was almost equal to the value of νC=O for unsubstituted biphenyl phenyl ketone. The decrease in the values of νC=O was observed for the compounds both in solution and in the crystalline state.

All of the compounds with methoxy and amino groups had a strong, sharp band in the 1595-1600 cm^{-1} region, which must be related to vibrations of the benzene rings.

The considerable difference observed in νC = O for amines in the crystalline state and in dioxane solutions is due, evidently, to intermolecular interaction of the NH$_2$ and C = O groups by hydrogen bonding, which decreases in dioxane solution.

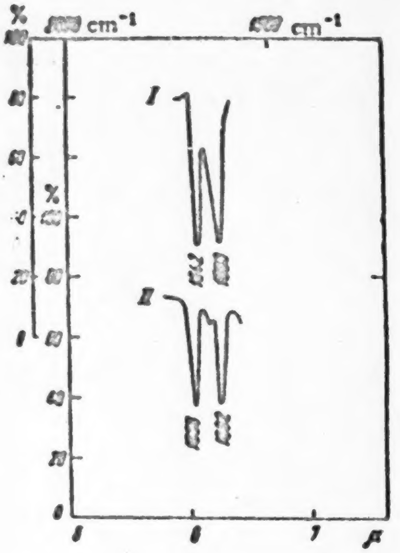


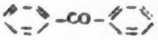
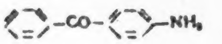
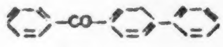
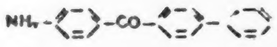
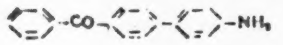
Fig. 1. Infrared spectra of biphenyl p-anisyl ketone (I) and p-methoxybiphenyl phenyl ketone (II).

The absorption bands of the C = O and NH$_2$ groups in the benzophenone amines coincided, since the absorption band of the valence vibration of a C = O group conjugated with the ring overlaps the band for the deformation vibration of an NH$_2$ group in an aromatic ring. Only in the case of IV, as a consequence merely of the insignificant interaction of these groups through the biphenyl radical (in dioxane solution), was a second band observed at 1622 cm^{-1}, which must be ascribed to deformation vibration of the NH$_2$ group (the vibration frequency of the NH$_2$ group in aniline is 1623 cm^{-1}).

Thus, from the IR data it can be concluded that the mutual effect of the groups in ketones II and IV, both in solution and in the crystalline state, is transmitted through the biphenyl system to a considerably less extent than in the corresponding phenyl ketones.

The data of the polarographic reduction are in complete agreement with this conclusion. As seen from Tables 1 and 2, the effect of the electron donor groups, OCH$_3$ and NH$_2$, transmitted through a benzene ring is apparent in a certain shifting of $\varphi_{1/2}$ in the direction of more negative values. At the same time, in ketones II and IV was observed a decrease in conjugation and an impedance in the transmission of the mutual effect through the biphenyl system.

TABLE 2

Compound	ν C=O, cm^{-1} crystals in polyfluoro-hydrocarbon	 solution in dioxane	δ NH$_2$, cm^{-1} (solution in dioxane)	$\varphi_{1/2}$, v (with respect to sat. cal. elec.) (in ammoniacal buffer)
	1661	1664	—	—1.360
	1635	1648	1648	—1.450
	1653	1660	—	—1.275
	1635	1650	1650	—1.380
	1652	1664	1622	—1.275

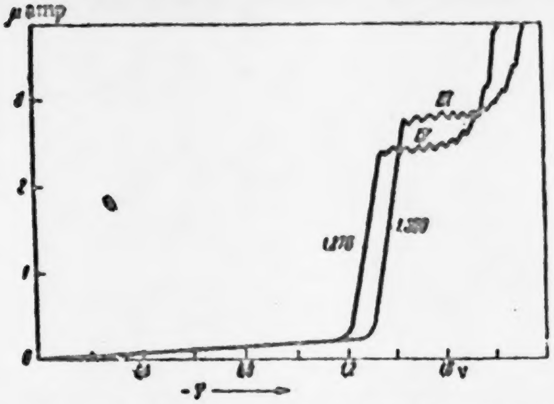


Fig. 2. Polarograms of biphenyl p-aminophenyl ketone (III) and p-aminobiphenyl phenyl ketone (IV) (with the addition of gelatin).

All of the data presented here on the impedance to the transmission of the mutual effect of the groups in ketones II and IV can be considered as indicating the noncoplanarity of biphenyl in these compounds, both in solution and in the crystalline state.

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KINETICS AND MECHANISM OF THE LIQUID-PHASE OXIDATION OF DIBENZYL AND DICYCLOHEXYLETHANE

S. R. Sergienko and N. Ya. Chernyak

(Presented by Academician A. V. Topchiev September 10, 1958)

Oxidation of the hydrocarbons was carried out in a glass, closed circulating system by bubbling oxygen through the liquid charge. The absorption of oxygen during the reaction was checked by the decrease in pressure in the system, and over a specific time interval a measured amount of oxygen was added to the system to bring the pressure up to the original value. At the conclusion of an experiment, the product from the reaction vessel was analyzed for content of the original hydrocarbon (by adsorptive separation on silica gel) and also for peroxides, acids, esters and alcohols, by potentiometric titration [1], and for benzaldehyde, by polarography [2].

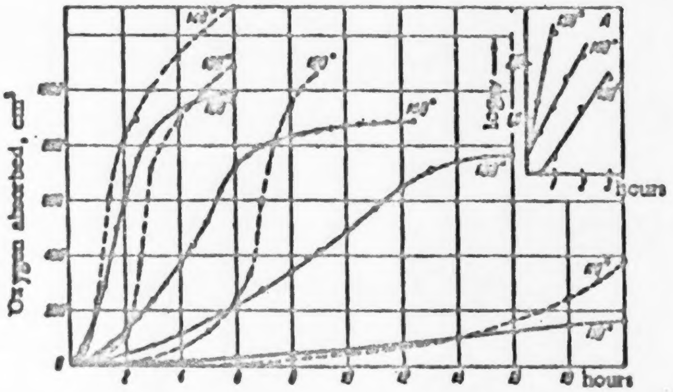


Fig. 1. A) Kinetics of the absorption of oxygen during oxidation of dibenzyl (solid curve) and dicyclohexylethane (dashed curve). B) Semilogarithmic plot of absorption curves for oxygen during oxidation of dibenzyl.

The oxidation of dibenzyl was carried out at temperatures of 110, 130, 140 and 150° (Fig. 1). The S-shaped curves and the fact that the semilogarithmic plots were linear in their initial portions indicate that the reaction proceeds by a chain mechanism with degenerate branching [3]. The value of the activation energy at the beginning of the oxidation process was 29 kcal/mole. Curves, presented in Figures 2 and 3, showing the consumption of original hydrocarbon and the accumulation of intermediate and final products of the oxidation of dibenzyl at 110 and 140° indicate the qualitative similarity of the course of the process at both temperatures. In the initial stage of the oxidation, practically nothing but peroxides were observed in the reaction products, the curves showing their formation practically coinciding with those for the absorption of oxygen and the consumption of dibenzyl, which is direct evidence of the formation of dibenzyl monohydroperoxide. The other oxidation products were formed as a result of the decomposition of this hydroperoxide and subsequent oxidation of of the resulting products, as is evidenced by the following experiment. Oxidation of dibenzyl was carried to the point of formation of the maximum amount of peroxide (3-hour period); nitrogen was then substituted for the oxygen in the system, and the heating was continued in the nitrogen atmosphere for 3 hours. Analysis of the reaction mixture obtained in this experiment showed that peroxides were absent, owing to their decomposition, and : there was a corresponding increase in benzaldehyde and alcohol. The acid content remained at the same level as during the 3-hour oxidation, since the oxygen required for the further oxidation of the benzaldehyde and alcohol formed by the decomposition of the peroxide was absent from the system.

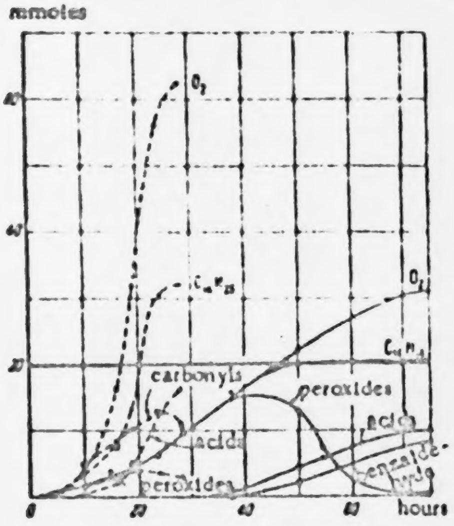
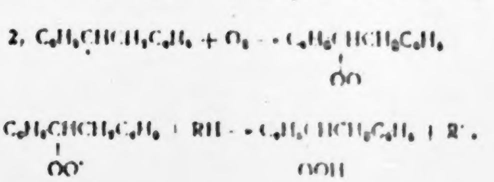


Fig. 2. Kinetics of the consumption of the original hydrocarbons and of the accumulation of intermediate products in the oxidation of dibenzyl (solid curve) and dicyclohexylethane (dashed curve) at 110°.

After the oxygen absorption slowed down, its consumption proceeded at a constant, very slow rate, an order of magnitude below the maximum. The addition to the reaction mixture of fresh dibenzyl up to the original amount, i.e., 10 g, at this stage of the oxidation did not increase the oxygen absorption rate; over a period of 110 hours, oxygen was absorbed at a uniform rate of ~10 ml/hour, while 4.5 g of dibenzyl was consumed during this period. From these experiments it follows that, first, inhibition of the oxidation was caused, not by consumption of the initial dibenzyl, but by the formation during the reaction of substances inhibiting oxidation, and, second, after the appearance of these substances in the oxidation products, the reaction proceeded by a different mechanism than in the initial period of oxidation. The addition to the initial dibenzyl of small amounts of tarry substances formed in proceeding oxidation experiments strongly inhibited the oxidation reaction (Fig. 4).

In addition to the experiments in which tar was added, experiments were carried out with the addition of different intermediate products of the oxidation reaction (Fig. 4). The addition of benzyl alcohol and benzaldehyde prior to the beginning of the reaction inhibited the oxidation of dibenzyl; the addition of these substances during the oxidation had no substantial effect on the course of the reaction. The addition of hydroperoxide prior to the beginning of the reaction strongly accelerated it. This effect of the accelerating action of the addition of peroxide also appeared when the addition was made at a stage when the oxidation reaction was already strongly inhibited. This latter circumstance indicates that just the hydroperoxide is responsible for the autocatalytic character of the process of the oxidation of dibenzyl in the first stage, and that the inhibitor formed during the course of the reaction acts on the peroxide radicals so that hydroperoxide cannot be formed. Consequently, after decomposition of the hydroperoxide available in the reaction products up to this time, the possibility of chain branching is lost, and, therefore, in the succeeding stage, the reaction does not proceed by branching and does proceed with a constant rate which is substantially lower than the rate for the chain-branching reaction.

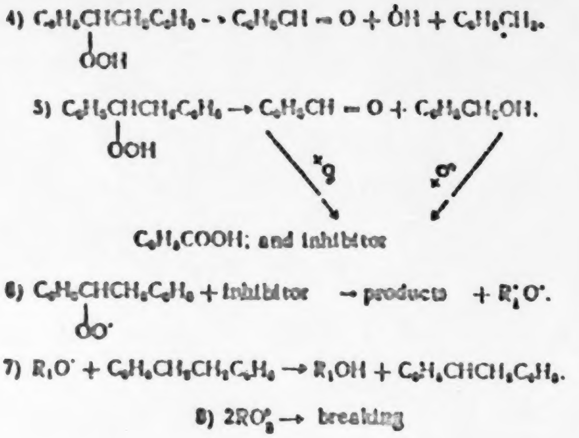
On the basis of the experimental data presented, the following radical-chain mechanism can be proposed for the oxidation of dibenzyl:



$$1)\ C_6H_5CH_2CH_2C_6H_5 \xrightarrow{+O_2} C_6H_5\dot{C}HCH_2C_6H_5 + HO_2;$$

$$2,\ C_6H_5\dot{C}HCH_2C_6H_5 + O_2 \rightarrow C_6H_5\underset{\substack{|\\ OO^{\cdot}}}{C}HCH_2C_6H_5$$

$$3)\ C_6H_5\underset{\substack{|\\ OO^{\cdot}}}{C}HCH_2C_6H_5 + RH \rightarrow C_6H_5\underset{\substack{|\\ OOH}}{C}HCH_2C_6H_5 + R^{\cdot}.$$



$$4)\ C_6H_5\underset{OOH}{CH}CH_2C_6H_5 \rightarrow C_6H_5CH=O + \dot{O}H + C_6H_5\dot{C}H_2.$$

$$5)\ C_6H_5\underset{OOH}{CH}CH_2C_6H_5 \rightarrow C_6H_5CH=O + C_6H_5CH_2OH.$$

$$\xrightarrow{x_9}\ C_6H_5COOH;\ \text{and inhibitor}\ \xleftarrow{x_9}$$

$$6)\ C_6H_5\underset{OO^{\cdot}}{CH}CH_2C_6H_5 + \text{inhibitor} \rightarrow \text{products} + R_1^{\cdot}O^{\cdot}.$$

$$7)\ R_1O^{\cdot} + C_6H_5CH_2CH_2C_6H_5 \rightarrow R_1OH + C_6H_5\dot{C}HCH_2C_6H_5.$$

$$8)\ 2RO_2^{\cdot} \rightarrow \text{breaking}$$

The oxidation of dicyclohexylethane was carried out at temperatures of 110, 120, 130 and 140°. This reaction also proceeded autocatalytically, developing in the initial period according to an exponential law (see Fig. 1). The value of the activation energy at the beginning of oxidation was 30.7 kcal/mole. The rate of

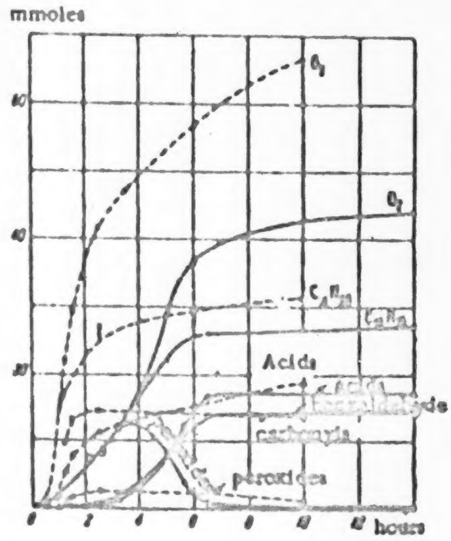


Fig. 1. Kinetics of the consumption of the initial hydrocarbons and accumulation of intermediate products of the oxidation of dibenzyl (solid curves) and dicyclohexylethane (dashed curves) at 140°.

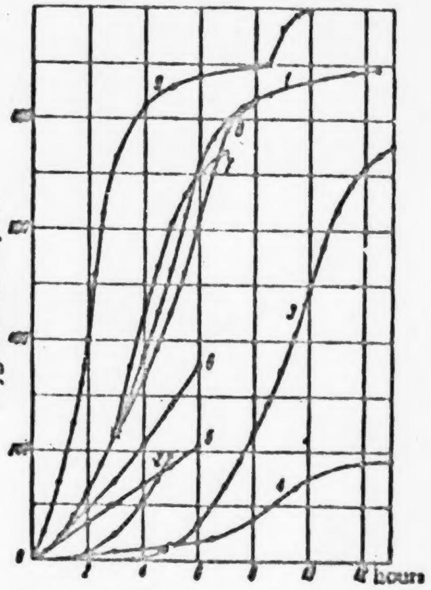


Fig. 4. Effect of the addition of intermediate products on oxygen absorption during the oxidation of dibenzyl at 140°: 1) without addition, 2) 0.025 g of tars prior to beginning of reaction, 3) 0.09 g of tars prior to beginning, 4) 1 g tars prior to beginning, 5) 10 mmole C_6H_5CHO prior to beginning, 6) 5.6 mmole $C_6H_5CH_2OH$ prior to beginning, 7) 6 mmole C_6H_5CHO 3 hours after beginning, 8) 5.6 mmole $C_6H_5CH_2OH$ 3 hours after beginning, 9) 9.5 mmole hydroperoxide prior to beginning and 1.3 mmole after slowing down of the reaction (the part of the curve marked with K).

oxygen absorption gradually decreased after attaining a maximum. It was possible to increase the rate somewhat by the addition into the reactor of fresh portions of the initial hydrocarbon, but, even in this case, the rate was almost 9 times lower than the maximum. This indicates that retardation of oxygen absorption was caused not so much by the consumption of the original hydrocarbon as by the appearance in the reaction products of substances inhibiting oxidation. However, the addition to the original hydrocarbon of 0.5 g of oxidation products insoluble in it (and in petroleum ether) had practically no effect on the kinetics of oxygen absorption; i.e., these products of the oxidation of dicyclohexylethane were not inhibitors of the reaction. In experiments with the addition to the original hydrocarbon of 0.1 g of tars obtained during the oxidation of dibenzyl, and which inhibited dibenzyl oxidation, there was a 5-hour induction period, after which oxidation proceeded at the usual rate. The dark color of the dicyclohexylethane, caused by the addition of the tar, gradually disappeared, which was direct evidence of the gradual consumption of the added tar in the induction period.

The small amount of peroxide compounds, in comparison with the amount obtained in the oxidation of dibenzyl, can apparently be explained by the lower thermal stability of dicyclohexylethane hydroperoxide in comparison with dibenzyl hydroperoxide.

The greater oxidation rate of dicyclohexylethane, in comparison with dibenzyl, at equal activation energies at the beginning of the process can apparently also be explained by an increase in reaction rate in the oxidation of dicyclohexylethane owing to the lower stability of the hydroperoxide.

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* Original Russian pagination. See C. B. translation.

ON THE MECHANISM OF THE OXIDATIVE CONVERSIONS OF METHYL ALCOHOL, FORMALDEHYDE AND FORMIC ACID IN THE VAPOR PHASE IN THE PRESENCE OF TIN VANADATE

B. V. Suvorov, S. R. Rafikov, V. S. Kudinova
and M. I. Khmura

(Presented by Academician B. A. Arbuzov October 3, 1956)

During the vapor-phase oxidation of alkylbenzenes over vanadium catalysts, considerable amounts of relatively low molecular weight compounds, chiefly formaldehyde, carbon monoxide, and carbon dioxide, are formed as by-products [1-3]. In a number of cases, especially during the oxidation of benzene homologs containing an isopropyl group [4], the formation of methyl alcohol, formic acid, and other substances may also be expected. The mechanism of the formation and further conversions of such "fragments" has been insufficiently studied. The available data unequivocally indicate only that of the compounds named above, the least stable under the conditions of vapor-phase oxidation in the presence of heterogeneous catalysts, including vanadium catalysts, are the lower aliphatic alcohols [5], during the oxidation of which the corresponding aldehydes and the products of complete combustion are formed in the greatest amounts, while acids are obtained in very low yield. The latter circumstance is connected with the instability of acids under the given conditions [6].

The aim of the present investigation was the study of the oxidative conversions of methyl alcohol, formaldehyde, and certain other oxygen-containing compounds, the formation of which is possible during the oxidation of alkylbenzenes. The work was carried out in a flow-type apparatus with a metallic reaction tube 1100 mm in length and 21 mm in diameter. The system used for feeding the charge stock has been described previously [3, 7]. The experiments were carried out at a contact time of 0.1-0.2 seconds, a feed rate of about 50 g per liter of catalyst per hour, and with a considerable excess of air (up to 60 liters STP per g of feed). Water was also introduced into the reaction zone in an amount of 350 g per cubic meter of air. Granular tin vanadate with a grain size of 3-5 mm diameter served as the catalyst.

Feed materials. The methyl alcohol had a b.p. of 62.5°/694 mm, n_D^{20} 1.3293, d_4^{20} 0.791. The formaldehyde was prepared by distillation of paraformaldehyde, and was used in the form of a 5.3% aqueous solution. The formic acid contained 8% water, and had a b.p. of 105°/695 mm, n_D^{20} 1.3681, and d_4^{20} 1.190. The hydrogen cyanide was introduced as a 6.3% aqueous solution of ammonium cyanide. The carbon monoxide was prepared by decomposition of formic acid, and contained 98.0% CO.

Analytical Methods. The gaseous reaction products passed from the reactor into a glass scrubber 1.5 meters high, which was wetted, by means of a Patrikeev pump [8], with a 10% aqueous solution of sodium hydroxide. The formaldehyde, hydrogen cyanide and carbon dioxide were absorbed in the scrubber liquid, and the effluent gas contained only carbon monoxide. The determination of the formaldehyde in the scrubber liquid was carried out iodometrically [9] and also by the dimedon method [10]. Hydrogen cyanide was determined by titration with silver nitrate in the presence of potassium iodide according to the method of Denigès [11]. In certain experiments, after neutralization of the alkaline absorbent with sulfuric acid and subsequent distillation, the hydrogen cyanide was separated in the pure form. Determination of carbon dioxide was carried out gravimetrically on the barium carbonate precipitate obtained by treating the scrubber liquid with aqueous barium hydroxide. For determination of carbon monoxide, a part of the gas leaving the scrubber was passed, after a preliminary washing with sulfuric acid, over Hopcalite. The carbon dioxide thus formed was collected in aqueous barium hydroxide.

The experimental results on the oxidation of methyl alcohol showed that it is completely reacted at a temperature of 310°. The main reaction products were formaldehyde and carbon monoxide (Fig. 1, A). On consideration of the sequence of their formation, it follows that formaldehyde is among the primary intermediate compounds. The formation of carbon monoxide is, apparently, a consequence of the decomposition of formaldehyde according to (I).

$$CH_2O \xrightarrow{-H^{\cdot}} \dot{C}HO \rightarrow CO + H^{\cdot} \qquad (I)$$

There are indications in the literature that the HCO radical decomposes completely into hydrogen and carbon monoxide at a temperature of about 100° [14].

The assumption stated above was also confirmed by the results of the oxidation of formaldehyde itself (Fig. 1, B). As seen from Figures 1, A and B, the course of the curves characterizing the product yields in the oxidations of methyl alcohol and formaldehyde are very similar. Formic acid was not observed in the reaction products in either case. This fact is explained not so much by a low stability of the formic acid under the given conditions as by the fact that in the early stages of the oxidation of the alcohol and the aldehyde, side reactions according to (I) and others are possible.

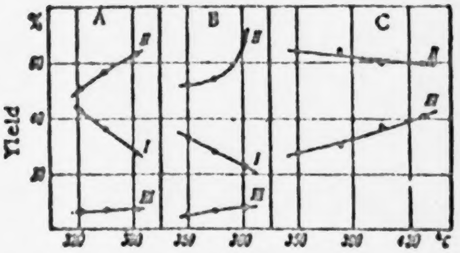
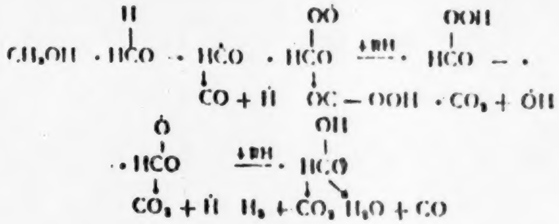


Fig. 1. Oxidation of methyl alcohol (A), formaldehyde (B), and formic acid (C) with moist air: I) formaldehyde, II) carbon monoxide, III) carbon dioxide.

The experimental data presented in Fig. 1, C show that a considerable amount of carbon dioxide up to 40% is formed during the oxidation of formic acid, while its yield does not exceed 10% in the oxidation of methyl alcohol and formaldehyde. Such a difference in yields of carbon dioxide provides a basis for the assumption that formic acid cannot be considered as a required intermediate product during the complete oxidation of methyl alcohol or formaldehyde. Apparently, the reaction proceeds in several directions. We note also that the high yield of carbon dioxide in experiments on the oxidation of formic acid cannot be interpreted as being the result of the previous oxidation of carbon monoxide. Experiments on the oxidation of carbon monoxide under comparable conditions (Fig. 2, B) showed that this reaction proceeds at a low rate over tin vanadate at temperatures up to 410°.

On the basis of the experimental data presented above, and using the peroxide and chain theories [12, 13], the following general scheme for the oxidation of methyl alcohol (and formaldehyde) can be proposed:



$$\begin{array}{l} CH_3OH \rightarrow \overset{H}{\overset{|}{HCO}} \rightarrow \underset{\displaystyle CO + \dot{H}}{\underset{\downarrow}{H\dot{C}O}} \rightarrow \underset{\displaystyle OC - OOH \rightarrow CO_2 + \dot{O}H}{\underset{\downarrow}{\overset{O\dot{O}}{\overset{|}{HCO}}}} \xrightarrow{+RH} \overset{OOH}{\overset{|}{HCO}} \rightarrow \\ \rightarrow \underset{\displaystyle CO_2 + \dot{H}}{\underset{\downarrow}{\overset{\dot{O}}{\overset{|}{HCO}}}} \xrightarrow{+RH} \underset{\displaystyle H_2 + CO_2 \quad H_2O + CO}{\underset{\downarrow \quad \searrow}{\overset{OH}{\overset{|}{HCO}}}} \end{array} \qquad (II)$$

With the aim of completely confirming the proposed scheme, it was of interest to investigate the oxidation of methyl alcohol under comparable conditions but in the presence of ammonia. Under these conditions, suppression of the reactions forming carbon monoxide and dioxide might be expected owing to the possibility of the reaction of the HCO radical with ammonia with the formation of formamide, which could easily undergo further conversion to hydrogen cyanide.

$$H\dot{C}O + NH_3 \xrightarrow{-H} HCONH_2 \xrightarrow{-H_2O} HCN \qquad (III)$$

It was preliminarily established that, under the oxidation conditions used and feeding 3-8 g of ammonia per g of feed, hydrogen cyanide does not undergo substantial change (Fig. 2, A). It was also shown that, in the temperature range investigated, carbon monoxide does not react with ammonia (Fig. 2, B), although it is known that this reaction proceeds with the formation of hydrogen cyanide at a higher temperature.

The experimental results on the oxidation of methyl alcohol in the presence of ammonia are presented in Fig. 2, D. They show that the main course of the reaction under the given conditions is the formation of hydrogen cyanide, the yield of which reaches 90%. It is characteristic that in the reaction of formic acid with ammonia under similar conditions, the yield of hydrogen cyanide does not exceed 50%. Consequently, the high yield of hydrogen cyanide during the oxidation of methyl alcohol (and formaldehyde) cannot be due to the intermediate formation of formic acid.

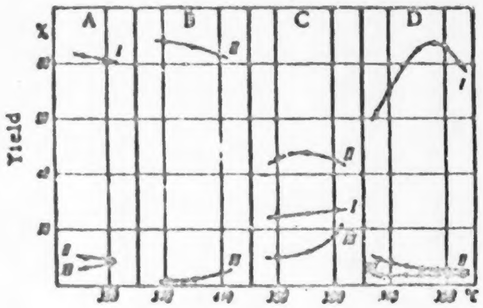


Fig. 2. Oxidation of hydrogen cyanide (A), carbon monoxide (B), formic acid (C), and methyl alcohol (D) with moist air in the presence of ammonia: I) hydrogen cyanide, II) carbon monoxide, III) carbon dioxide.

The results of the last experiments thus confirm the mechanism presented above of the successive conversions of methyl alcohol and formaldehyde under the conditions of vapor-phase oxidation over vanadium catalysts.

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A NEW REACTION FOR THE SUBSTITUTION OF ALCOHOLIC HYDROXYL BY FLUORINE AND ITS USE

A. I. Titov, G. N. Veremeev, V. V. Smirnov
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(Presented by Academician I. N. Nazarov October 16, 1956)

One problem in the investigation of organofluorine compounds is the discovery of methods for the direct substitution of fluorine for alcoholic hydroxyls. The well-known reactions for the preparation of alkyl halides, particularly the action of hydrogen fluoride and fluorine compounds of phosphorus on alcohols, are not very applicable for this purpose [1, 2]. Information of a general nature on the trends in this field [3, 4] require confirmation.

In 1942, one of us and A. N. Baryshnikova demonstrated the possibility of substituting fluorine for alcoholic hydroxyl in a single stage by converting ethylene chlorohydrin to 1,2-chlorofluoroethane by refluxing it with a mixture of benzenesulfonyl fluoride and potassium fluoride. Our investigations demonstrated the general nature of this reaction, which proceeds according to the equation:

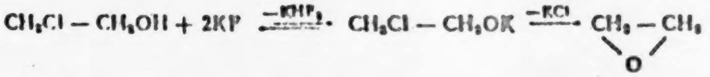
$$ROH + R'SO_2F + 2KF = RF + R'SO_3K + KHF_2 \qquad (1)$$

its mechanism was also demonstrated. It was found that the reaction proceeds through successive stages.

The first stage of the reaction is the formation of an alcoholate according to:

$$ROH + 2KF \rightleftarrows ROK + KHF_2. \qquad (2)$$

as is confirmed by the solubility of potassium fluoride in alcohols, by the alkaline nature of such solutions, by the ease with which the more "acid" halohydrins enter into Reaction (1), by a comparison of the dissociation constants of H_2F_2, water, and alcohols, and by a number of other facts. In particular, we consider that the discovery of I. L. Knunyants and co-workers [5] that ethylene oxide is formed by the action of potassium fluoride on ethylene chlorohydrin:



$$CH_2Cl-CH_2OH + 2KF \xrightleftharpoons{-KHF_2} CH_2Cl-CH_2OK \xrightarrow{-KCl} \underset{\diagdown\,O\,\diagup}{CH_2-CH_2} \qquad (2')$$

is indisputable proof of the intermediate formation of alcoholates in the reactions studied by us. We also observed the formation of ethylene oxide during the preparation of ethylene fluorohydrin by the method of Hoffman [6].

The next step is the acylation of the alcoholate by the sulfonyl fluoride with the formation of the alkyl sulfonate :

$$ROK + R'SO_2F \rightarrow R'SO_2OR + KF. \quad (3)$$

which was proved directly by the isolation of these esters from the reaction mixture in the first phases of the synthesis. Quite recently, as we learned after the conclusion of the investigation, Pattison [7] indicated, in a very general way, the use of potassium fluoride for the preparation of certain alkyl sulfonates by the action of sulfonyl fluorides on alcohols in the presence of potassium fluoride. The partial formation of sulfonates by the action of sulfonyl fluorides on alcohols without the participation of potassium fluoride is also possible.

The last stage involves the alkylation of the potassium fluoride :

$$R'SO_2OR + KF \rightarrow RF + R'SO_2OK. \quad (4)$$

as was previously known from the work of Helferich [8] and of Razumovsky and Fridenberg [9] and again confirmed by us for a number of cases.

Summation of the left and right sides of Equations (2), (3) and (4) leads to the final scheme of the synthesis (1).

Side reactions forming ethers, unsaturated compounds, their polymers, etc., can parallel Reaction (1).

The new method was successfully used for the preparation of alkyl fluorides and substituted alkyl fluorides.

Of particular interest are the experiments on the preparation of 1,2-difluoroethane by the new reaction. In recent works of Henne [10, 11], this material was described as an unstable compound with a b.p. of 10-11°, which decomposes at 0° into butadiene and hydrogen fluoride, and which is readily hydrolyzed by water to ethylene glycol. These properties are paradoxical, even in the organofluorine series. From Henne's report, it seemed impossible to expect the successful preparation of 1,2-difluoroethane by the new reaction. However, its preparation did not present particular difficulty.

1,2-difluoroethane was a completely stable substance with a b.p. of 26°, and it possessed the usual properties of fluoroparaffins, in particular, stability toward hydrolysis. Its boiling point falls into place in the series:

$$CH_2Cl - CH_2Cl\ (84°),\ CH_2Cl - CH_2F\ (52°),\ CH_2F - CH_2F\ (26°).$$

The same difluoroethane was synthesized by alkylation of KF with β-fluoroethyl benzenesulfonate.

In the case of ethylene chlorohydrin, along with the major product, 1,2-chlorofluoroethane, Reaction (1) led to appreciable formation of 1,2-dichloroethane and, apparently, 1,2-difluoroethane. The preparation of dichloroethane was due to the reaction of the intermediately formed β-chloroethyl benzenesulfonate with potassium chloride, which resulted from the reaction of this same ester and ethylene chlorohydrin with KF, for example :

$$CH_2Cl - CH_2OSO_2C_6H_5 + KF \rightarrow CH_2F - CH_2OSO_2C_6H_5 + KCl \quad (5)$$

$$CH_2Cl - CH_2OSO_2C_6H_5 + KCl \rightarrow CH_2Cl - CH_2Cl + C_6H_5SO_3K \quad (6)$$

$$CH_2F - CH_2OSO_2C_6H_5 + KF \rightarrow CH_2F - CH_2F + C_6H_5SO_3K \quad (7)$$

The ease with which Reactions 6 and 7 occur was shown directly. These conclusions are also applicable to explain the formation of dichloroethane during alkylation of potassium fluoride with β-chloroethyl benzenesulfonate in the experiments of Razumovsky.

We present a description of some experiments.

I. 20 g of methyl alcohol, 80 g of benzenesulfonyl fluoride, and 58 g of potassium fluoride were refluxed for 7 hours with stirring, and the liberated methyl fluoride was collected over 50% $CaCl_2$ (7.5 liters – over 60% of theoretical). The gas, purified with H_2SO_4, was identified by molecular weight (34.0) and fluorine content (55.5%). The latter was determined by repeatedly bubbling the gas through an alcoholic solution of sodium hydroxide, measuring the decrease in volume and titrating F^-.

The reaction with ethyl alcohol occurred with greater difficulty; ether and ethyl benzenesulfonate were isolated as by-products. Alkylation of KF with the ethyl sulfonate also gave identical C_2H_5F and a mixture of olefins.

II. 32 g of ethylene fluorohydrin, 80 g of benzenesulfonyl fluoride, and 64 g of KF were heated on a bath (180-190°) with a dephlegmator which permitted distillation of the 1,2-difluoroethane (20-25°). The yield of product was about 50%. After drying and distillation, the 1,2-difluoroethane had the following properties: b.p. 26-28.2°; d_4^{18} = 1.024; n_D^{18} = 1.3014; M 65.52 (cryoscopically), 66.10 (Meyer method) (theoretical, 66.05); F, 56.6% (theoretical, 57.5).

Splitting off of a fluorine ion in aqueous and alcoholic NaOH proceeded slowly (1-2% in an hour at 70°) and somewhat more rapidly in the presence of acid (up to 6%). Similarly to dichloro- and chlorofluoroethane, it mixed with fuming HNO_3 and separated on dilution with water.

The β-fluoroethyl benzenesulfonate had the following properties: b.p. 161-162° (3 mm); d_4^{18} = 1.3407, n_D^{18} = 1.5104. F, determined by titration after a half-hour boiling of 1 g of the ester with 150 ml of 2% aqueous alcoholic NaOH, was 7.9% (theoretical, 9.3%). It is interesting that the ester mixed with 1 – 10 parts of CCl_4, but the solution stratified on further dilution. Alkylation of KF with the ester gave the 1,2-difluoroethane described above with a yield close to theoretical. Recently, Edgell and Parts [12], without isolating the 1,2-difluoroethane "in substantia," demonstrated the probability of its formation by infrared spectra of the vapors formed in a similar reaction of fluoroethyl toluenesulfonate with potassium fluoride.

III. 40 g of ethylene chlorohydrin, 60 g of $C_6H_5SO_2F$, and 50 g of KF were heated for 6 hours on a bath (180-200°) with distillation of the reaction products; the following fractions were separated from the products: 1st, 25-40°, 1.3 g; 2nd, 45-60°, 12.9 g; 3rd, 65-75°, 2.5 g; 4th, over 75°, 8 g. 1,2-fluorochloroethane (I) was isolated from the second fraction: b.p. 51-53°; d_4^{17} = 1.184, n_D^{17} = 1.3955, % Cl, 43.0; % F, 24.0. N-fluoroethyl-3-nitrophthalimide (II), m.p. 105°, was prepared from (I) by heating with potassium nitrophthalimide to 180-200° (10 hours); fluorine was not split off during this reaction. (II) prepared from (I) synthesized according to Razumovsky, was identical. 1,2-dichloroethane was isolated from the higher fractions; it was also obtained by heating β-chloroethyl benzenesulfonate with potassium chloride (b.p. 82°; d_4^{20} = 1.253, n_D^{18} = 1.4465). From the residue remaining after carrying out the reaction, β-chloroethyl benzenesulfonate was isolated (b.p. 174° at 6 mm; d_4^{17} = 1.361, n_D^{17} = 1.531).

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ON THE QUESTION OF THE MONOTROPIC TRANSFORMATION OF SPODUMENE

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Among the numerous lithium minerals, spodumene, more than the others, has been the object of various investigations. The greatest interest and the greatest difficulties have been in the study of its thermal properties—fusibility and transitions at high temperatures.

In 1901-1903, Doelter [1] determined the melting point of spodumene, and, after many experiments, he settled on a value of 1080-1090°. These data are much too low, and are obsolete. Newer and more reliable investigations on spodumene have been carried out by Endell and Riecke [2] and by Ballo and Dittler [3].

Endell and Riecke established that when spodumene is heated to 920° its density remains unchanged, but the powdered mineral has the density of a glass after a 6-hour heating at 980°; the change in density was observed in the range of 20° (d = 3.147) to 1320 (d = 2.367).

Observations on the birefringence of the mineral after cooling, and also on a heated microscope stage, showed that the powder heated at 950° for 6 hours is anisotropic (in grains of 300-700 μ) or mainly isotropic (5-30 μ).

A study of the index of refraction permitted the conclusion that if spodumene has an average index of refraction of n' = 1.66 at 20° and this value is retained up to 920°, then at a higher temperature there is an instantaneous change in the index of refraction, and it takes on the value of 1.519 ± 0.004 (at 980°), which then remains constant.

Thus, the regions of instantaneous (discontinuous) changes in the spodumene properties considered coincide in the rather narrow range of 920-980°, which might be called the thermal transition range of spodumene (a region of the transition of one modification into another).

Endell and Riecke erroneously called this region a region of melting.

Regardless of the conclusions arrived at by these authors, they did not establish the existence of a more symmetrical modification of spodumene which appears at temperatures close to 950° and which is accompanied by a sharp increase in volume, 24%. Only the monoclinic form of spodumene has been found in nature, and its transition into this unusual modification, which differs so sharply in many physical properties, is irreversible.

Brun [4] first pointed out the discrepancies in the facts and conclusions of Endell and Riecke, and he considered that the change in structure of spodumene with considerable expansion takes place at 1010°; during the change, the crystals of the mineral retain their form, but crumble to a very fine dust with a slight jar.

Ballo and Dittler [3] did not confirm the observation of Endell and Riecke of the disappearance of birefringence in heated natural spodumene; on the contrary, even above 1200° they observed clear birefringence, which is contrary to the idea of an isotropic form of spodumene at a high temperature. However, determining the change in specific gravity of spodumene after heating, Ballo and Dittler finally established the presence of a high temperature modification, and evaluated it as polymorphic and irreversible. They showed that the transition rate of spodumene is very high at high temperatures; in 1.75 hours at 1050° 90% of the spodumene was converted into the new modificiation, while 0.5 hour was required at 1200°. Ballo and Dittler proposed for natural spodumene the designation α-spodumene (by analogy with the formation of high temperature α-quartz). This proposal is correct, since β-spodumene is not distinguished from natural α-spodumene in composition, but only in physical and optical properties; consequently, all spodumene minerals found in nature must be considered as the metastable phase with respect to the β-form.

The practical consequence of investigations of the transition of spodumene is the use of roasting of spodumene-containing rocks for enrichment in lithium [5, 6, 7].

However, it must be noted that, for the preparation of β-spodumene, the time of heating the α-spodumene is determined not only by the source of the mineral, but also by the batch of ore (other conditions being equal), since pure spodumene is not encountered in nature, but rather very different stages of weathering are represented in this mineral at the present time.

As a result of hypergenetic changes, kaolinization of spodumene increases and albitization also proceeds, and, as a result, the heating curve of spodumene shows additional effects, so that, as shown by S. G. Tumanov and G. N. Maslennikova [8], thermal analysis can be used for the determination of the degree of kaolinization of spodumene. This is undoubtedly of practical interest, although it seems to us that thermal analysis will not be sufficiently accurately precise for the case under consideration. We investigated strictly the conversion of spodumene, not the products of its conversion, and in this connection we investigated the effect of heating rate and of different impurities on the temperature of the monotropic transition of α-spodumene to the β-modification.

TABLE 1

Composition of α-Spodumene Samples in Wt. %

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Li_2O	Σ
1	64.04	31.18	Trace	0.22	Trace	0.01	Trace	5.18	100.57
2	65.34	30.10		0.20		0.01	0.14	4.70	100.40
3	66.34	27.58		0.22		0.12	0.12	6.05	100.43

In Table 1 is presented the chemical analysis of three samples of spodumene on which the present work was carried out (the composition in wt. % is expressed on the basis of the mineral after calcination). The spodumene was sorted under a binocular microscope and was freed from extraneous minerals.

TABLE 2

Regions of α → β-transition of Spodumene

Sample No.	Heating rate, degrees/min.	Spodumene transition region, °C
1	11	995–1050
1	21	1005–1070
2	10	1025–1070
2	23	1028–1100
3	11	990–1035
3	23	995–1070

By a general spectral analysis, manganese and titanium were found in all samples, copper in Samples 1 and 3, and tin in Sample 2.

The temperature effects for the α → β-transition, obtained from heating curves recorded at two heating rates, are presented in Table 2.

As seen from Table 2, with an increase in heating rate the temperature at which the transition begins increases and the transition interval widens. This is in agreement with the observation of Meissner [9], who, it seems, first pointed out the effect of heating rate on the monotropic transition of spodumene. In general, the effect of heating rate must always be considered in the solution of a number of problems by means of thermal analysis; unfortunately, importance is not attached to this in many investigations.

In Table 3 are presented data on the effect of the addition of pure quartz and potassium sulfate on the temperature of the α → β-transition of spodumene at a constant heating rate (~11 degrees/minute). From a comparison of the data of Table 3 with those of Table 2 it is seen that SiO_2 and K_2SO_4, mechanically mixed with the spodumene, lowered the temperature of the α → β-transition, and with an increase in the content of the added component its effect increased. It should be noted that the effect of the potassium sulfate was less.

TABLE 3

Effect of Added SiO_2 and K_2SO_4 on the Temperature of the α → β-Transition of Spodumene

Sample No.	Amount added, wt. %	Transition region, °C
1	5 (SiO_2)	975–1010
1	20 (SiO_2)	915–1000
1	5 (K_2SO_4)	1005–1035
1	50 (K_2SO_4)	985–990
2	5 (SiO_2)	990–1035
2	20 (SiO_2)	925–1020
2	5 (K_2SO_4)	1005–1035
2	50 (K_2SO_4)	975–1010
3	5 (SiO_2)	980–1005
3	20 (SiO_2)	945–1000
3	5 (K_2SO_4)	965–995
3	50 (K_2SO_4)	950–990

It is interesting that the impurities contained in the spodumene itself, i.e., the isomorphous replacements for lithium which, according to Gabriel [10], can number up to 10 (and probably even more), also have a very substantial effect on the temperature of the monotropic α → β-transition of spodumene.

The mechanism of this effect is not completely clear; however, if the data of Tables 1 and 2 are compared, it can be seen that the spodumene richer in lithium undergoes α → β-transition at a lower temperature.

This is in agreement with the observations of Endell and Riecke [2], who worked with the richest spodumene samples ever found (7.62% Li_2O) and obtained the lowest value for the temperature of the monotropic transition.

Such an effect of the elements replacing lithium in spodumene on the transition temperature region is quite characteristic, but uncommon, if it is assumed that replacement of lithium by many elements is isomorphous [10], since usually the formation of solid solutions based on a component possessing a polymorphous transition lowers the temperature of this transition. It is evident that the study of the nature of the replacement of lithium in spodumene by one element or another must have separate interest.

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ON THE ELECTROLYTIC DISSOCIATION OF COMPLEX COMPOUNDS OF TIN AND ANTIMONY

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(Presented by Academician I. I. Chernyaev October 25, 1956)

The source of electrical conductivity in systems consisting of nonconducting components is connected with an acid-base reaction which results in the formation of complex compounds of a salt-like nature [1-3]. On mixing halides of tetravalent tin and trivalent antimony (arsenic) with aliphatic monocarboxylic acids and their esters, electrolytes are formed having the general formulas :

$$SnX_4 \cdot 2RCOOR',\ SnX_4 \cdot 4RCOOR',\ SbX_3 \cdot RCOOR',\ 2SbX_3 \cdot RCOOR',$$

where R' is hydrogen or an aliphatic radical and X is Cl or Br.

Electrolytic dissociation of these compounds, in our opinion, proceeds as:

$$1.\ SnX_4 \cdot 2RCOOR' + RCOOR' \rightleftarrows [SnX_4(RCOO)_2]R'^{-} + RCOO_2'^{+}.$$

$$2.\ SnX_4 \cdot 2RCOOR' + 2RCOOR' \rightleftarrows [SnX_4(RCOO)_2]^{--} + 2RCOOR_2'^{+}.$$

$$3.\ SbX_3 + RCOOR' \rightleftarrows [SbX_2 \cdot RCOOR']^{+} + X^{-}.$$

$$4.\ 2SbX_3 + RCOOR' \rightleftarrows [SbX_2RCOOR']^{+} + [SbX_4]^{-}.$$

It follows from Equations 1 and 2 that in the complex compounds $SnX_4 \cdot 3RCOOR'$ and $SnX_4 \cdot 4RCOOR'$ the organic molecule enters into the composition of both anion and cation, and the tetravalent tin halide enters only into the anion. In complex compounds of trivalent antimony the organic molecule enters into the composition of the cation (Equations 3 and 4).

In order to confirm the scheme of the electrolytic dissociation of these complex compounds, ion migration was studied in the systems

$$SnCl_4 - CH_3OH,\ SnCl_4 - CH_3COOH \quad SnCl_4 - CH_3COOC_2H_5,\ SbCl_3 - CH_3COOH,$$

in which the organic component contained the isotope C^{14}.

The results of experiments on the electrolysis of solutions of stannic chloride in methyl alcohol, acetic acid, and ethyl acetate showed that in all cases stannic chloride, under the influence of an electric current, migrated to the anode, and the organic molecule migrated both to the anode and to the cathode. Thus, we established that stannic chloride enters into the composition of the anion, and CH_3OH, CH_3COOH and $CH_3COOC_2H_5$ enter into the composition of both the cation and the anion. These results are in agreement with Equations 1 and 2.

While our work was being carried out, two articles [6, 7] devoted to this question appeared. The authors of these papers proposed their own schemes of the electrolytic dissociation. Common to these schemes was the assumption that the formation of the complex compounds is a reaction of insertion, i.e., the molecule of the organic substance enters into the composition of the complex cation. However, our experiments on ion migration in systems in which the organic component contained the isotope C^{14} refutes these schemes.

Experiments on ion migration in the system $SbCl_3 - CH_3COOH$, in which the CH_3COOH contained C^{14}, showed that the CH_3COOH migrates only to the cathode. In agreement with Equations 3 and 4, the results of the experiments show that complex compounds of antimony (and arsenic) trihalides with organic oxygen-containing substances, in contrast to compounds of these same organic substances with tin tetrahalides, are products of insertion reactions [1].

Desiring to determine the fate of molecules of an organic substance under the influence of an electric current, in experiments on the electrolysis of the system $SbCl_3 - CH_3COOH$ we also added a dye — methyl red — to the solution along with the C^{14}-tagged CH_3COOH. In this way it was established that, as we expected, methyl red migrates in the same direction as the tagged CH_3COOH, i.e., to the cathode. Thus, from the experiments with the dye it was graphically evident that the molecule of organic substance migrates to the cathode, i.e., it enters into the composition of the cation, as expressed by Equations 3 and 4.

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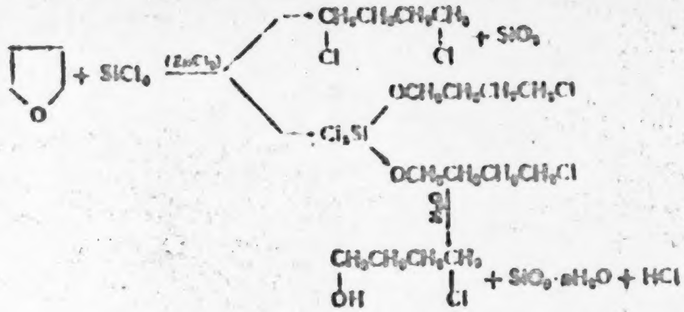

The reaction between tetrahydrofuran and silicon tetrachloride was carried out in the following manner. In a flask, fitted with a reflux condenser, was placed 1 mole of tetrahydrofuran, 1 mole of $SiCl_4$, and only 1 g of anhydrous zinc chloride. The reaction mixture was refluxed for 5 hours, and then, after distillation of the unreacted $SiCl_4$, the remainder was fractionated under reduced pressure.

Fraction I: b.p. 50-51° (9 mm); 18 g; d_4^{20} 1.1294 and n_D^{20} 1.4518. Found MR_D 30.92; calculated for $C_4H_8Cl_2$ MR_D 30.41. This fraction, obtained in a yield of about 15%, was 1,4-dichlorobutane.

Fraction II distilled, with slight decomposition, in the range 150-185° (5 mm). It was a colorless liquid which fumed in air. Hydrolysis of this fraction was carried out in a flask fitted with a stirrer, a dropping funnel, and a reflux condenser. Into an ethereal solution of the fraction was slowly added, from the dropping funnel, a weak solution of soda. The hydrolysis products were extracted several times with ether. After drying with anhydrous potassium carbonate and distillation of the ether, the hydrolysis products were distilled under reduced pressure. From the hydrolysis were obtained silicic acid and 4-chloro-1-butanol with the following properties: b.p. 80-81° (10 mm); d_4^{20} 1.0883 and n_D^{20} 1.4515. Found MR_D 28.02; calculated for C_4H_9ClO MR_D 27.93. The yield of 4-chloro-1-butanol, which was obtained in an amount of 65 g, was about 65% calculated on the original tetrahydrofuran.

Thus this investigation established that the reaction of tetrahydrofuran with silicon tetrachloride in the presence of anhydrous zinc chloride as a catalyst gives 1,4-dichlorobutane and di(δ-chlorobutoxy)dichlorosilane. This reaction can serve as a method for the preparation of oxygen-containing organosilicon compounds and chloro-substituted aliphatic alcohols.

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ON THE REACTION OF TETRAHYDROFURAN WITH SILICON TETRACHLORIDE

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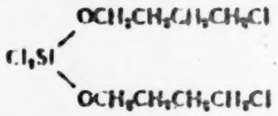
It has been established by a number of investigators that the tetrahydrofuran ring can undergo cleavage under the influence of various halogen-containing agents with the formation of 1,4-dihalo derivatives of aliphatic hydrocarbons. Thus, Froebe and Hochstätter [1], Starr and Hixon [2], and Fried and Kleene [3], in a study of the action of hydrogen halides on tetrahydrosylvan, tetrahydrofuran and 2,5-dimethyltetrahydrofuran, found that as a result of ring cleavage the 1,4-dihalo derivatives of butane, pentane, and hexane are formed. By the action of HBr on α-propyl-, α-butyl-, and α-benzyltetrahydrofuran in acetic acid solution at 120-125°, Paul [4], obtained the corresponding 1,4-dibromoheptane, 1,4-dibromooctane, and 1-phenyl-2,5-dibromopentane. Wilson [5] investigated the cleaving action of HBr in the presence of acetic anhydride on tetrahydrofuran and a number of its functional derivatives and also on tetrahydropyran. As a result, he obtained bromo derivatives of butane or pentane. Cloke and Ayers [6] showed that the action of phosphorus tribromide on tetrahydrofuran forms 1,4-dibromobutane with a yield of 53%. In a patent, Grimm and Schimpfle [7] reported the preparation of 1,4-dichlorobutane in high yields (up to 90%) by the action of phosgene on tetrahydrofuran at 45-125° and in the presence of catalysts capable of splitting off acids and water (Al_2O_3, $ZnCl_2$, MoO_3, activated carbon, etc.).

We found [8, 9] that the tetrahydrofuran ring is cleaved by the action of aluminum chloride and bromide, titanium tetrachloride, and antimony pentachloride. This results in the formation of 1,4-dichlorobutane. In the present work, we investigated the action of silicon tetrachloride on tetrahydrofuran. It was found that, in the absence of catalysts, tetrahydrofuran and silicon tetrachloride do not react, even on heating for 8 hours. However, under the catalytic influence of anhydrous zinc chloride, the reaction between these compounds proceeds rather rapidly and leads to the formation of 1,4-dichlorobutane and an organosilicon compound to which the following structure is ascribed:



$$Cl_2Si\begin{matrix}\nearrow OCH_2CH_2CH_2CH_2Cl\\ \searrow OCH_2CH_2CH_2CH_2Cl\end{matrix}$$

This organosilicon compound is readily hydrolyzed by water with the evolution of heat, being converted to 4-chloro-1-butanol and silicic acid. If the reaction is carried out with equimolar amounts of tetrahydrofuran and silicon tetrachloride, all of the tetrahydrofuran and about half of the silicon tetrachloride enter into the reaction. This fact substantiates the correctness of the structure proposed by us for the organosilicon compound. Thus, as a result of the reaction between tetrahydrofuran and silicon tetrachloride, 1,4-dichlorobutane and di(δ-chlorobutoxy)dichlorosilane are formed as major products:

INVESTIGATION OF TAUTOMERISM AND GEOMETRIC ISOMERISM IN SOME ARYLHYDRAZONES BY THE POLAROGRAPHIC METHOD

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It is known that phenylhydrazones when dissolved in alcohol are partially converted into aliphatic-aromatic azo compounds [1,2]. The possibility has been suggested of the existence of still another tautomeric form with a structure of the enhydrazine type [3-5], but up to now proof of this has not been achieved.

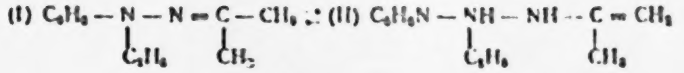
There is an extensive literature on the stereoisomerism of arylhydrazones; many of the compounds of this class have been isolated in two forms [6,7]. Attempts to obtain various derivatives of both isomers have not succeeded [7,8], but the appearance of two forms by analogy with the oximes has been considered geometric isomerism. However N. V. Khromov-Borisov [9] has recently shown that there cannot be a complete analogy between the stereoisomerism of the oximes and the hydrazones. Recently the stereoisomerism of the colored nitrophenylhydrazones has been studied by the spectroscopic method [10-12].

Thus the tautomerism and stereoisomerism of the arylhydrazones has as yet been inadequately investigated.

Since it is known that tautomeric forms and stereoisomers are reduced at different potentials at the dropping mercury electrode, the polarographic method was chosen for the present work in order to follow the changes taking place when arylhydrazones are dissolved in alcohol.

Polarograms were made of methanol solutions of the phenylhydrazones of acetone, methyl ethyl ketone, methyl isopropyl ketone, cyclohexanone, acetophenone, p-chloroacetophenone, acetaldehyde and benzaldehyde, keeping the solutions in the dark. A borate buffer with pH of 7,2 served as the carrier, the concentration of the solution studied was ~ 0,6 – 1,2 · 10^{-3} M, and the polarograms were made at 20° on a type M8-2000 visual polarograph. The half-wave potentials ($e_{1/2}$) were determined graphically and were referred to a saturated calomel electrode. For each solution a family of polarograms was obtained that characterized the changes taking place in the solutions in a given time. Regularities were discovered in the variations of the curves; thus, in polarograms of the phenylhydrazones of the aliphatic ketones and cyclohexanone in the course of time the initial waves of $e_{1/2}$ about -1,40 v disappeared, waves of $e_{1/2}$ ~ -0,7v appeared and grew, and waves of $e_{1/2}$ = -1,08v appeared, grew, and then diminished. These last waves usually divided, each into two new waves of which one – with the less negative potential – gradually disappeared. The initial waves of solutions of the phenylhydrazones of the aldehydes and the aliphatic-aromatic ketones were at less negative potentials than -1,4 v.

The polarograms obtained were interpreted as follows. Supplementary polarograms were made for methanol solutions of azobenzene as a standard azo form, and of the ethylphenylhydrazone of acetone as a compound incapable of producing an azo form. Under our conditions azobenzene was reduced at -0,6v, i.e., the waves of the azo forms of arylhydrazones must be in the neighborhood of this potential. Winkel and Siebert [13], using the polarograph, showed that under the influence of light azobenzene in alcohol solution is converted into the labile syn-form, which in the dark rearranges to the stable anti-isomer. Therefore the appearance observed by us of waves at potentials of -0,68 and -0,75 v, their division into two waves with $e_{1/2}$ -0,63, -0,78 v and -0,84, -0,97 v, and the subsequent growth of the latter in the polarograms of the phenylhydrazones studied correspond to the formation of a mixture of the stereoisomers of the azo form and the gradual disappearance in the dark of the labile syn-isomer. In the polarograms of the ethylphenylhydrazone of acetone there are only two waves at potentials -1.20 and -1.50 v which correspond to the two possible tautomers (I) and (II) of this compound:



$$(I)\ C_6H_5-\underset{C_6H_5}{N}-N=\underset{CH_3}{C}-CH_3 \rightleftarrows (II)\ C_6H_5N-\underset{C_6H_5}{NH}-NH-\underset{CH_3}{C}=CH_2$$

The phenylhydrazone of benzaldehyde cannot form an enhydrazine and in the polarograms of its alcohol solution, besides the wave of the free aldehyde, there are two wave pairs, one pair of which must belong to the syn- and anti-isomers of the azo form ($e_{1/2}$ = -0.56 and -0.99 v), and the other to the two isomers of the hydrazone form ($e_{1/2}$ = -1.08 and -1.20 v).

Thus it was found that potentials from -1.40 to -1.55 v correspond to the waves of the enhydrazines and from -1.0 to -1.30 to the waves of the hydrazones.

The families of polarograms obtained by us were interpreted to show that the phenylhydrazones of acetone, methyl ethyl ketone, methyl isopropyl ketone, and cyclohexanone and the ethylphenylhydrazone of acetone, contrary to the generally accepted hypothesis, are not hydrazones, but in the free state have the syn-enhydrazine type of structure. The phenylhydrazone of methyl ethyl ketone in alcohol in the dark also forms the anti-isomer of the enhydrazine form. The phenylhydrazones of the aldehydes and also of acetophenone and p-chloroacetophenone in the free state have the anti-hydrazone structure. All of the compounds studied, except the ethylphenylhydrazone of acetone, in alcohol solution undergo a tautomeric conversion to a mixture of azo compounds according to the following scheme:

enhydrazine → hydrazone → azo compound

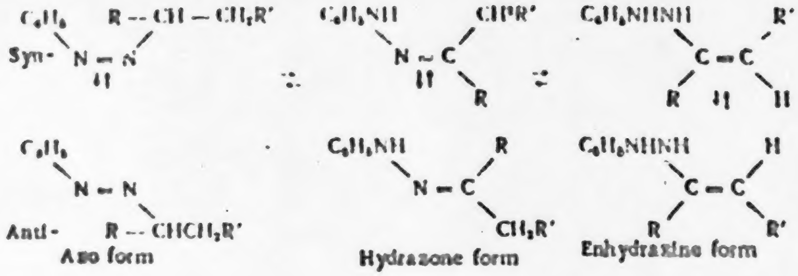
In Table 1 are given the half-wave potentials found for the tautomers and stereoisomers and the energies for their interconversions, calculated from the potential differences by the method of Winkel and Sibert [13].

TABLE 1

Compounds	Azo form				Hydrazone form				Enhydrazine form		
	a	b	c	d	a	b	c	e	a	b	e
$PhNHNH_2 + CH_3COCH_3$	0.66	0.84	8.8	15.4	1.00		—	10.0	1.45		—
$PhNHNH_2 + CH_3COC_2H_5$	0.68	0.87	8.7	20.2	1.08	1.30	10.1	13.6	1.44	1.55	5.1
$PhNHNH_2 + CH_3COCH(CH_3)_2$	0.73	0.84	10.1	13.6	1.00	1.19	8.7	16.6	1.44	—	—
$PhNHNH_2 + C_6H_{10}O$	0.76	0.87	9.7	13.8	1.20		—	6.2	1.20		—
$PhNHNH_2 + CH_3COC_6H_5$	0.48	0.84	15.2	14.4	1.15	1.28	6.6	—	—	—	—
$PhNHNH_2 + CH_3COC_6H_4Cl_n$	0.64	0.82	12.9	17.6	1.08	1.27	9.7	—	—	—	—
$PhNHNH_2 + C_6H_5CHO$	0.56	0.80	15.2	16.9	1.18	1.20	5.5	—	—	—	—
$PhNHNH_2 + CH_3CHO$	0.50	0.78	12.9	19.2	1.05	1.15	6.0	11.5	1.35		—
$PhNHNH_2 + (CH_3)_2CHCHO$	—	—	—	—	—	1.20	—	—	—	—	—

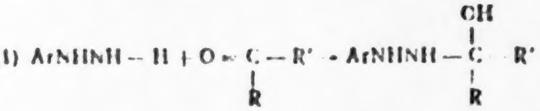
Note. a) $e_{1/2}$ for syn-isomers. b) $e_{1/2}$ for anti-isomers. c) energy for conversion syn → anti (Cal per mole) d) energy for conversion hydrazone → azo compound (Cal per mole) e) energy for conversion enhydrazine → hydrazone (Cal per mole)

Polarographic investigation of a series of phenylhydrazones showed that in general they can exist in three tautomeric forms, each of which has stereoisomers:



The fact that the tautomeric forms can be reduced indicates the presence in their molecules of conjugated bonds, since it is known that isolated multiple bonds under these conditions either are not reduced at all or only at considerably more negative potentials.

The different structure of the arylhydrazones of aldehydes and aliphatic-aromatic ketones on the one hand and of aliphatic and alicyclic ketones on the other hand can be explained in the following way. The reaction of an arylhydrazine with a carbonyl compound proceeds in two stages [14]. First, addition takes place at the carbonyl double bond:

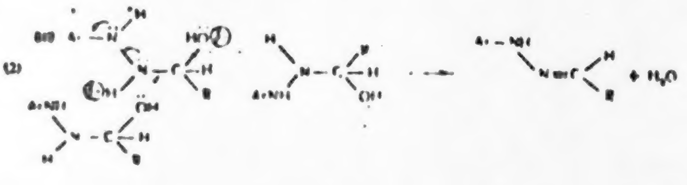
(1) 

$$ArNHNH-H+O=\underset{R}{\underset{|}{C}}-R'\rightarrow ArNHNH-\overset{OH}{\overset{|}{\underset{R}{\underset{|}{C}}}}-R'$$

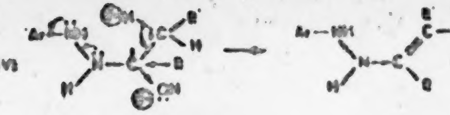
The further conversion of the intermediate carbinol depends upon the structure of the original carbonyl compound. Thus if an aldehyde is used, a carbinol results in which the influence of the free electron pair of the nitrogen atom conjugated with the bonds of the aromatic ring on the free electron pair of the second nitrogen atom is stronger than the influence of the electrons of the oxygen atom. Because of πPP-bonding the N–H linkages are weakened and one of them becomes conjugated with the polar C–O bond.

It is known [15] that in highly conjugated systems parallelism, i.e., trans-configuration at the bonds, occurs. Therefore free rotation around the bond between the nitrogen and the aliphatic carbon of the carbinol is hindered and structure III is energetically the most advantageous.

The polarity of the carbinol molecules results in orientation and drawing together, and as they approach each other the molecules will interact through the end atoms of the σσ-bond system. The electron distribution in the systems results in the formation of water and the anti-isomer of the hydrazone:

(2) 

The presence of a second alkyl group on the carbon atom of the intermediate carbinol obtained from a ketone changes the interaction of the bonds: it strengthens the polarization of the C–O bond and weakens the interaction of the latter with the N–H bond, but creates conditions favorable to conjugation with the C–H bond of the neighboring carbon atom. The most advantageous structure from the energy viewpoint is IV, in which free rotation around the C–C bond is hindered.



(IV) (V)

The subsequent intermolecular elimination of water, proceeding according to a scheme analogous to (3), gives the syn-isomer of the anhydrazine (V). The alicyclic ketones react in the same way; but if R is an aryl group, the second stage of the reaction of the arylhydrazine with the aliphatic-aromatic ketone proceeds as with an aldehyde. Evidence of the stepwise course of the reaction is found in the fact that upon mixing the arylhydrazine and the carbonyl compound, at first heat is evolved while the mixture remains homogeneous, and only after some time does instantaneous turbidity appear and the separation of water occur. The latter circumstance indicates the chain mechanism of the second stage.

It has long been known that the phenylhydrazone of acetaldehyde can be prepared in two forms, which have been assumed to be stereoisomers. When these isomers are dissolved in a large amount of solvent, a mutual interconversion occurs with the preferential formation of the higher melting form [7].

Using the polarograph, we found these forms of the phenylhydrazone of acetaldehyde to be tautomers, not stereoisomers; i.e., the substances with m.p. 57°, obtained by reaction of its components in ether in the cold or from the second form by treatment with an alcoholic solution of SO_2, is the anti-isomer of the phenylhydrazone ($\epsilon_{1/2}$ = 1.18 v in dioxane), while the substance with m.p. 98-101° proved to be β-phenylhydrazinoethylene ($\epsilon_{1/2}$ = = −1.88 v).

We further succeeded in obtaining by the method of Thile and Pickard [16] two isomers of the phenylhydrazone of benzaldehyde and showed that the isomer with m.p. 114-6° is the syn-form ($\epsilon_{1/2}$ = −1.08 v) and the isomer with m.p. 182° the anti-form ($\epsilon_{1/2}$ = −1.18 v) of the hydrazone. Our investigations of the tautomerism and stereoisomerism of the arylhydrazones are being continued.

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THE REACTION OF ORGANOHYDROXYSILANES WITH ISOCYANATES

SYNTHESIS OF SILICOORGANIC URETHANES

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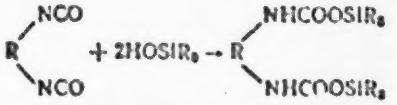
From the literature it is known that the reaction of alcohols with isocyanates proceeds without the formation of by-products. Wurtz[1] first showed that the reaction is accompanied by the migration of a hydrogen atom of the alcoholic hydroxyl group to the nitrogen atom of the isocyanate group:

$$R-N=C=O+HOR\rightarrow RNHCOOR$$

In the work described here we undertook to investigate the reaction of organohydroxysilanes with isocyanates. The starting materials used in the study of the reaction were triethylhydroxysilane, diethylpropylhydroxysilane, diethylbutylhydroxysilane, and metatoluylenediisocyanate [4-methyl-m-phenylene ester of isocyanic acid].

In the course of the investigations it was first established that the reaction of the isocyanates with trialkylhydroxysilanes proceeds in a manner analogous to the corresponding reaction with alcohols and can be represented as follows:



$$R\left\langle\begin{matrix}\text{NCO}\\ \text{NCO}\end{matrix}\right. + 2HOSiR_3\rightarrow R\left\langle\begin{matrix}\text{NHCOOSiR}_3\\ \text{NHCOOSiR}_3\end{matrix}\right.$$

By this reaction scheme the following silicoorganic urethanes were obtained and characterized: toluylene-2,4-bis-carboamine-triethylsilane [4-methyl-m-phenylene-dicarbamate of triethylsilanol], toluylene-2,4-bis-carboamine-diethylpropylsilane [4-methyl-m-phenylenedicarbamate of diethylpropylsilanol], and toluylene-2,4-biscarboaminediethylbutylsilane [4-methyl-m-phenylenedicarbamate of diethylbutylsilanol]. All the silicoorganic urethanes obtained were white, crystalline substances soluble in benzene, toluene, and ether, and very susceptible to hydrolysis. Their properties are given in Table 1, along with the properties of other new silicoorganic compounds, which are not described in the literature.

EXPERIMENTAL

1. Synthesis of diethylbutylchlorosilane. In a 2.5 to 3-liter three-necked flask fitted with a reflux condenser, mechanical stirrer, dropping funnel, and thermometer, were placed 48.6 g of magnesium turnings, 1000 ml of anhydrous ethyl ether, and 0.6 to 1 ml of ethyl bromide. From the dropping funnel 274 g of butyl bromide was added dropwise. After the introduction of a small amount of the butyl bromide, the reaction mixture was stirred at room temperature for 20 to 30 minutes. After the reaction started, the further addition of butyl bromide was carried out with the temperature of the reaction mixture not higher than 30 to 35°. Following its introduction, stirring at room temperature was continued for 1.0 to 1.5 hours, after which the reaction mixture, freed from the remaining magnesium mechanically or by filtering through glass wool, was poured off into a dropping funnel.

Into the emptied three-necked flask was poured 314 g of diethyldichlorosilane (b.p. 128 to 130°, d_4^{20} = = 1.1074) and 400 ml of anhydrous ether, after which the butyl magnesium bromide was added with constant stirring. The reaction mixture was heated on the water bath for 8 to 10 hours. The reaction products were then filtered with suction and the residue was washed with several portions of ether. After distilling off the ether from the extract . . J the solution, and subsequent repeated fractionation of the reaction products, 215 g of a substance was isolated which had the following constants: b.p. 181-182°/744mm; n_D^{20} = 1.4410; d_4^{20}= 0.8985; MR found 52.46; MR calc. for $C_8H_{19}SiCl$ 53.06.

Found %: C 53.75, 53.54; H 10.46, 10.47; Si 14.97, 15.31; Cl 19.95, 19.85. $C_8H_{19}SiCl$ Calculated %: C 53.78; H 10.64; Si 15.68; Cl 19.88.

On the basis of the analytical data, the substance with b.p. 181 to 182°/744mm is diethylbutylchlorosilane. The yield of this compound was 60% of theoretical, based on diethyldichlorosilane.

2. Synthesis of diethylbutylhydroxysilane. In a three-necked flask were placed 100 g of diethylbutylchlorosilane (b.p. 181-182°/744mm; d_4^{20} 0.8985; n_D^{20} 1.4410), 500 ml of anhydrous ether, and several drops of phenolphthalein. The contents of the flask were cooled to -5°. While the reaction mixture was vigorously stirred, 1N aqueous sodium hydroxide was added from a dropping funnel until a presistent light pink color appeared. The temperature of the reaction mixture did not exceed +2°. The contents of the flask were poured into a separatory funnel and the ether and the water layers were separated. The water layer was washed with several 70 to 100 ml portions of ether. The ether layer and ether extracts were combined and dried over potassium carbonate for 25 to 30 minutes. After distilling off the ether and subsequently fractionating in vacuo, 63 g of a substance was isolated with the following constants: b.p. 190/744 mm; n_D^{20} 1.4390; d_4^{20} 0.8608; MR found 48.80; MR calc. for $C_8H_{20}SiO$ 49.37.

Found %: C 60.06, 60.20; H 12.6, 12.40; Si 17.45, 17.13. $C_8H_{20}SiO$ Calculated %: C 60.00; H 12.50; Si 17.50.

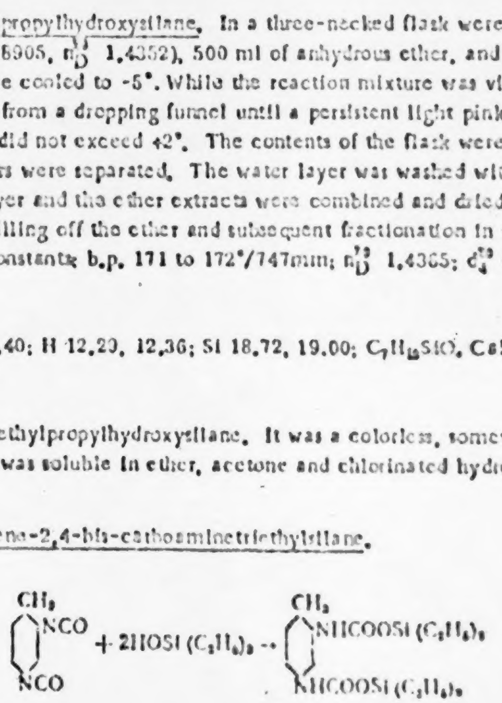
This compound was diethylbutylhydroxysilane. It was a colorless, somewhat viscous liquid with a pleasant camphor-like odor. It was soluble in ether, acetone, and chlorinated hydrocarbons, but almost insoluble in water.

3. Synthesis of diethylpropylhydroxysilane. In a three-necked flask were placed 100 g of diethylpropylchlorosilane (b.p. 160°; d_4^{20}0.8905, n_D^{20} 1.4352), 500 ml of anhydrous ether, and several drops of phenolphthalein. The contents of the flask were cooled to -5°. While the reaction mixture was vigorously stirred, 1N aqueous sodium hydroxide was added from a dropping funnel until a persistent light pink color appeared. The temperature of the reaction mixture did not exceed +2°. The contents of the flask were poured into a separatory funnel and the ether and water layers were separated. The water layer was washed with several 70 to 100 ml portions of ethyl ether. The ether layer and the ether extracts were combined and dried over potassium carbonate for 25 to 30 minutes. After distilling off the ether and subsequent fractionation in vacuo, 63 g of a substance was isolated with the following constants: b.p. 171 to 172°/747mm; n_D^{20} 1.4365; d_4^{20} 0.8598; MR found 44.40; MR calc. for $C_7H_{18}SiO$ 44.71.

Found %: C 57.64, 57.40; H 12.20, 12.36; Si 18.72, 19.00; $C_7H_{18}SiO$. Calculated %: C 57.53, H 12.32, Si 19.17.

This compound was diethylpropylhydroxysilane. It was a colorless, somewhat viscous liquid with a pleasant, camphor-like odor. It was soluble in ether, acetone and chlorinated hydrocarbons, but almost insoluble in water.

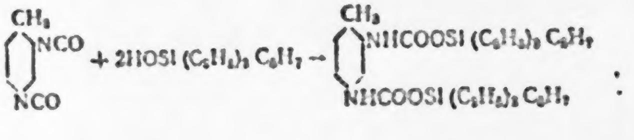
4. Synthesis of toluylene-2,4-bis-carboaminotriethylsilane.



A mixture of 43.5 g (0.25 mole) of m-toluylenediisocyanate (m.p. 21°; d_4^{20} 1.2235; n_D^{20} 1.5663 and 132 g (1.0 mole) of triethylsilanol (b.p. 80°/30 mm; n_D^{20} 1.4320; OH-group content 12.8%) was placed in a round-bottom flask fitted with a condenser having a calcium chloride tube at the end. The contents of the flask were heated on an oil bath for an hour at 80 to 85°, after which they were allowed to stand in the flask overnight. The next day the reaction mixture was transferred to a filter and repeatedly washed with gasoline, then, after drying in the air, was recrystallized from hot toluene. A white powder was obtained, m.p. 152 to 153°. Mol.wt. found 459.4; calc. 438.

Found %: C 57.61, 57.48; H 8.53, 8.44; Si 12.70, 12.38, N 6.35, 6.48. $C_{21}H_{38}N_2Si_2O_4$. Calculated %: C 57.53; H 8.67; Si 12.78; N 6.39.

5. Synthesis of toluylene-2,4-bis-carboaminediethylpropylsilane.

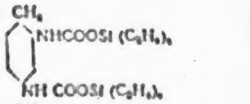
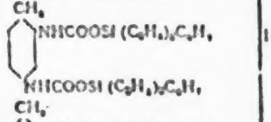
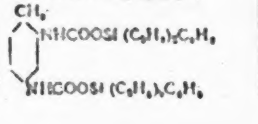


A mixture of 43.5 g (0.25 mole) of m-toluylenediisocyanate (m.p. 21°; d_4^{20} 1.2235; n_D^{20} 1.5663); and 73 g (0.5 mole) of diethylpropylhydroxysilane (b.p. 171 to 172°/747 mm; n_D^{20} 1.4365; d_4^{20} 0.8580; OH-group content 11.7%) was placed in a round-bottomed flask fitted with a condenser having a calcium chloride tube at the end.

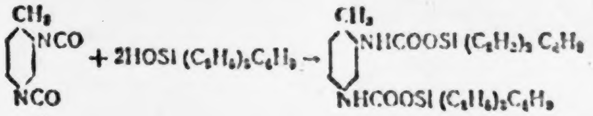
The contents of the flask were heated on an oil bath for an hour at 80 to 85°, after which they were allowed to stand in the flask overnight. The next day the reaction mixture was transferred to a filter and repeatedly washed with gasoline (at first with small portions of gasoline) and then, after drying in the air, was recrystallized from hot toluene. A white powder was obtained with m.p. 140-141°. Mol.wt. found 460.3; calc. 466.

Found %: C 58.97, 58.95; H 9.08, 9.12; Si 12.02, 11.70; N 6.2, 6.3. $C_{23}H_{42}N_2Si_2O_4$. Calculated %: C 59.22; H 9.01; Si 12.01; N 6.00.

TABLE 1

Name of compound	Formula	M.p. °C	B.p. °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.
Diethylbutylchlorosilane	$(C_2H_5)_2C_4H_9SiCl$		181–183 (744)	0.8985	1.4410	52.46	53.03
Diethylbutylhydroxysilane	$(C_2H_5)_2C_4H_9SiOH$		190 (744)	0.8620	1.4300	49.80	49.87
Diethylpropylhydroxysilane	$(C_2H_5)_2C_3H_7SiOH$		171–172 (747)	0.8608	1.4365	44.49	44.71
Toluylene-2,4-bis-carboaminetriethylsilane	 CH₃ NHCOOSi (C₂H₅)₃ NH COOSi (C₂H₅)₃	152–153					
Toluylene-2,4-bis-carboaminediethylpropylsilane	 CH₃ NHCOOSi (C₂H₅)₂C₃H₇ NHCOOSi (C₂H₅)₂C₃H₇	140–141					
Toluylene-2,4-bis-carboaminediethylbutylsilane	 CH₃ NHCOOSi (C₂H₅)₂C₄H₉ NHCOOSi (C₂H₅)₂C₄H₉	104–106					

6. Synthesis of toluylene-2,4-bis-carboaminediethylbutylsilane.



A mixture of 43.5 g (0.25 mole) of m-toluylenediisocyanate (m.p. 21°; d_4^{20} 1.2385; n_D^{20} 1.5663); and 80.0 g (0.50 mole) of diethylbutylhydroxysilane (b.p. 190°/744mm; n_D^{18} 1.4390; d_4^{20} 0.8508; OH-group content 10.6%) was placed in a round bottomed flask fitted with a condenser having a calcium chloride tube at the end.

The contents of the flask were heated on an oil bath for an hour at 80 to 85°, after which they were allowed to stand in the flask overnight. The next day the reaction mixture was transferred to a filter and repeatedly washed with gasoline (at first with small portions of it), and then, after drying in the air, was recrystallized from hot toluene. A white powder was obtained with m.p. 104 to 106°. Mol.wt. found 479; calc. 494.

Found %: C 60.66, 60.52; H 9.42, 9.47; N 6.05, 6.13; Si 11.3. $C_{25}H_{46}N_2Si_2O_4$. Calculated %: C 60.72; H 9.31; N 5.66; Si 11.33.

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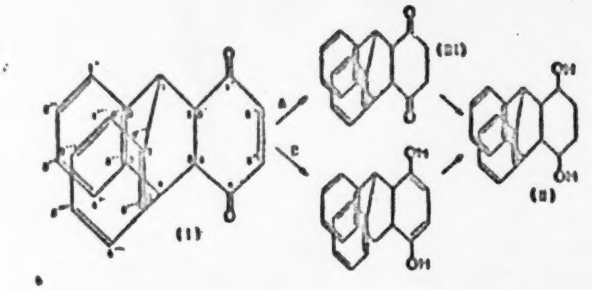
ON THE STEREOCHEMISTRY OF CATALYTICALLY ACTIVE COMPLEXES

Academician A. A. Balandin and E. I. Klabunovsky

As shown previously [1], during the catalytic hydrogenation of 2,3-dihydro-(2,3; 5′,6′) (5,6;5″,6″) (7, 8; 5‴, 6‴)-tribenzobicyclo-(2,2,2)-octadien-5,7-dione-1′,4′ (I), which is a derivative of triptycene, in the presence of skeletal nickel catalyst at atmospheric pressure in dioxane medium at 45°, three moles of hydrogen are absorbed, and the corresponding hexahydroaromatic diol is formed: 1′, 2′, 3′, 4′, 5′, 6′-hexahydro-(2,3; 5′, 6′) (5,6;5″,6″) (7, 8; 5‴, 6‴)-tribenzobicyclo-(2,2,2)-octadiene-5,7-diol-1′,4′ (II). The kinetic curve of the absorption of hydrogen in this process shows a sharp break after the absorption of one mole of hydrogen (33.3% conversion), which indicates the selective nature of the hydrogenation. However, the stages through which the reaction proceeds still have not been experimentally clarified, since two routes, A and B, can be visualized for the reaction:



According to multiplet theory [2], during successive hydrogenations over nickel catalyst the olefinic bond must be hydrogenated first and only then the carbonyl bond, since the height of the energy barrier (−E) of the first reaction (−E = 2.9 kcal.) is lower than that of the second (−E = 10.1 kcal).

In agreement with these theoretical concepts, which are supported by numerous experimental data [3], it would be expected that in compound I the double bond C = C is hydrogenated first with the formation of the corresponding hexahydroaromatic diketone (III), and then the two keto groups are hydrogenated leading to the formation of the hexahydroaromatic diol (II).

In order to clarify the reaction mechanism, we carried out the hydrogenation of compound (I), which was prepared according to reference [4]; m.p. 207° (decomp.).

Found %: C 83.90, 84.01; H 4.95, 4.94. $C_{20}H_{14}O_2$. Calculated %: C 83.91; H 4.89.

The hydrogenation was carried out in a thermostated rocking autoclave (TS-17 thermostat) at 45° and atmospheric pressure over skeletal nickel catalyst (0.35 g) in a medium of freshly distilled dioxane (in the absence of peroxides). The experimental method and preparation of the catalyst has been described in reference [1].

After the absorption of one mole of hydrogen, which, in a parallel experiment, corresponded to a break in the kinetic curve drawn by plotting the rate (ml H_2 STP per minute), against the extent of reaction in % (see arrow in Figure 1), the product was filtered from the catalyst and recrystallized from a mixture of dioxane and toluene (1 : 1). The investigation showed that the product obtained was product III – 1',2',3',4',5',6'-hexahydro-(2,3;5',6') (5,6; 5'',6'') (7,8; 5''', 6''')-tribenzobicyclo-(2,2,2)-octadiene-5,7-dione-1',4' – a compound which has not been described in the literature. In the pure form, it consists of yellowish crystals with m.p. 182-3° (decomp.).

Found %: C 83.10, 82.90; H 5.47, 5.53. $C_{20}H_{16}O_2$. Calculated %: C 83.33; H 5.55.

Product III did not undergo reactions of a quinoid structure (compound (I) was colored by the action of KI + I_2 + KOH), did not undergo reactions of an olefinic double bond, did not form the phenylurethan, and did not react with maleic anhydride. The reaction of III with 2,4-dinitrophenylhydrazine gave the mono-2,4-dinitrophenylhydrazone, which crystallized readily from ethanol-chloroform mixture (1 : 2), m.p. 188-9°.

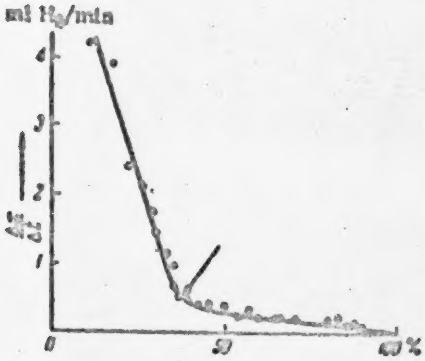


Fig. 1.

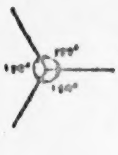
Found %: N 12.28, 12.41. $C_{26}H_{20}N_4O_5$. Calculated %: N 11.69.

The formation of monophenylhydrazones by 1,4-diketones has been reported in the literature [5].

The data obtained confirm the prediction of multiplet theory that hydrogenation of compound I proceeds by route A of the scheme presented above. In addition, these results serve as one more example of the experimentally widely vindicated succession of hydrogenolysis of bonds over nickel catalyst, as revealed by multiplet theory [2,3].

Multiplet theory permits the construction of stereochemical models of the active complexes of the reactions considered above.

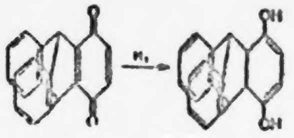
According to this theory, owing to the small radius of action of valence-chemical forces, the molecules come into contact with the catalyst at their reacting atoms, which determines the orientation of the molecules on the catalyst. From this, scale models of the hydrogenation of various derivatives of triptycene are presented below. The molecules have a complex configuration: the six-membered rings joined to the central bicyclic system are disposed at an angle of 120° to each other, which can be represented on a plane as follows:



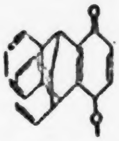
Therefore, the molecule cannot be entirely disposed on a plane surface. In the models of Figure 2, the molecules of the triptycene derivatives are oriented to the surface of the catalyst in accordance with the above-indicated requirements of multiplet theory. Here, model a corresponds to the hydrogenation of triptycenehydroquinone, which was discussed in reference [1]. The basis of this model is the sextet mechanism of hydrogenation. In Figure 2, b is shown a model of the hydrogenation of compound (III), the model of this doublet reaction being constructed in accordance with the model constructed earlier [6]. The existence of the reaction III → II and of the model of Figure 2 corresponding to it, necessarily follows from the fact that reaction I → III proceeds, as shown in the present communication, and that the reaction I → II occurs, as observed in reference [1].

In Figure 2, c is shown a model of the hydrogenation of compound I. This model corresponds to an edge disposition of the six-membered ring on the catalyst surface [2]. It is seen from Figure 2 that the molecules in a and b are not placed on the surface in view of steric hindrance, and the hydrogenation must proceed on projections of the catalyst, while in the case of c the hydrogenation can proceed on the surface of the catalyst.

In the case of the hydrogenation of triptycenequinone, described in reference [1], the considerable O–O interatomic distance in the quinone indicates that the hydrogenation proceeds not by molecular hydrogen, but by atomic hydrogen, in agreement with



the requirements of the theory [6]. Apparently, the hydrogenation proceeds through the semi-hydrogenated form, which is joined to the nickel through only one oxygen just as in the hydrogenation of ketones [7]. In the present case, the radical corresponding to the semi-hydrogenated form has a semi-quinhydrone structure:



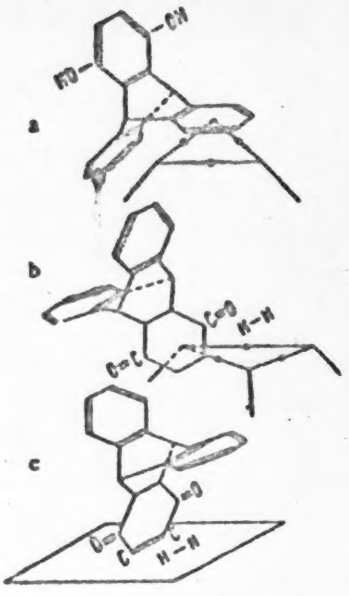


Fig. 2.

It is well known that, under specific conditions, similar radicals are very stable; their solutions are intensely colored.

However, during the hydrogenation of triptycenequinone, the yellow solution gradually decolorized, which indicates that, if such a radical is formed, it is not desorbed into the solution, but undergoes here, on the surface of the catalyst, further chemical transformation. The results obtained are important to an understanding of the nature of catalytically active centers.

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ON CONDITIONS FOR THE ADDITION OF AROMATIC AMINES TO ACRYLONITRILE

A. F. Bekhli

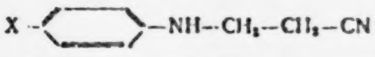
(Presented by Academician I. N. Nazarov, November 26, 1956)

It is well known that the addition of aromatic amines to acrylonitrile can be carried out in the presence of acid catalysts (acetic acid and its amine salts, acetic anhydride, and salts of inorganic acids with aromatic and aliphatic amines [1-5]).

The reaction does not proceed on refluxing aromatic amines with acrylonitrile without a catalyst, and the unchanged materials can be recovered from the reaction mixture [6].

In an investigation of this reaction, we attempted to prepare β-phenylaminopropionitrile by heating the components in a sealed tube at 165-170°; however, the addition product was not formed, and the original components were recovered from the reaction mixture. Using an aromatic amine hydrochloride in place of the amine and refluxing with acrylonitrile, we confirmed the negative results of Cymerman-Craig et al. [6].

TABLE 1

β-Arylaminopropionitrile 

X	B. p., °C/? mm	M. p., °C	Yield, %	Reference	N %	
					found	calculated
H	199—200/35—37	49—50	19	(2)	—	—
CH_3	204—206/32	104	25	(8,9)	—	—
Cl	199—200/7—8	74—75	53	(9,10)	—	—
OC_2H_5	225/22	74.5—75	62.1	—	14.58 14.78	14.73
OCH_3	219—223/21	62	69.5	(11,12)	—	—

However, we found that heating the indicated components in an aqueous medium leads to the formation of β-phenylaminopropionitrile [7]. We also established that ammonium chloride has no catalytic effect when refluxing aniline with acrylonitrile in an anhydrous medium; in the presence of water NH_4Cl catalyzes this reaction, and β-phenylaminopropionitrile is obtained in a yield of about 60%.

These data permit the assumption that a necessary condition for the addition of aromatic amines to acrylonitrile is the presence of protons in the reaction mixture. Therefore, we considered it possible to carry out the addition of an aromatic amine to acrylonitrile without the addition of acid catalysts but in water, which, being an ionic medium itself, contains protons.

Experiments carried out by us completely confirmed this assumption. It was found that, in fact, aromatic amines do add to acrylonitrile on heating in water. We carried out experiments with five aromatic amines (aniline, p-toluidine, p-chloroaniline, p-anisidine, and p-phenetidine) under the same conditions, and in all cases we obtained the corresponding β-arylaminopropionitrile (Table 1).

Apparently, the yield of β-arylaminopropionitrile depends on the solubility of the original amine in water. We presume that the mechanism of the reaction consists in the formation of an intermediate carbonium ion which can act as the alkylating agent [8].

The method of preparation of β-arylaminopropionitriles by cyanethylation of aromatic amines in aqueous medium can have practical significance, and makes this class of compounds readily available.

EXPERIMENTAL

Addition of aromatic amines to acrylonitrile in water without a catalyst. The aromatic amine (0.05 mole) was refluxed with acrylonitrile (0.1 mole) in water (5 ml) for 11.5 hours. The reaction mixture was extracted with benzene. The benzene solution was washed with water and dried with potassium carbonate. After distillation of the volatile products, the residue was distilled under vacuum.

The following aromatic amines were used: aniline, p-toluidine, p-chloroaniline, p-anisidine, p-phenetidine. The results of the experiments are presented in Table 1.

Reaction of aniline with acrylonitrile in anhydrous medium. a) 9.3 g (0.10 mole) of aniline and 6.0 g (0.11 mole) of acrylonitrile were heated in a sealed tube for 8.5 hours at 165-170°. The following fractions were obtained by distillation of the mixture: 1) 5.0 g, b.p. 76° (acrylonitrile), 2) 8.5 g, b.p. 122° at 90 mm (aniline), 3) 0.4 g, boiling up to 115° at 3 mm, a yellowish oil which distilled with decomposition and contained aniline. We were unable to crystallize this oil.

b) 4.7 g (0.05 mole) of aniline, 2.8 g (0.05 mole) of acrylonitrile, and 1.4 g (0.025 mole) of ammonium chloride were refluxed for 7.5 hours. After the usual treatment of the reaction mixture and distillation of the volatile products, fractionation of the residue under vacuum gave only aniline (3.2 g), b.p. 73° at 3-4 mm.

Reaction of aniline with acrylonitrile in aqueous medium in the presence of NH_4Cl. In an experiment similar to that described under "b" but carried out in the presence of water (5 ml), two fractions were separated from the residue remaining after distillation of the highly volatile products. 1) 0.9 g, boiling to 100° at 7 mm, aniline; 2) 4.3 g, 58.9% of theoretical, b.p. 173-175° at 7 mm, m.p. 49° (from alcohol), β-phenylaminopropionitrile.

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ALKYLATION OF AROMATIC COMPOUNDS WITH DIENIC HYDROCARBONS

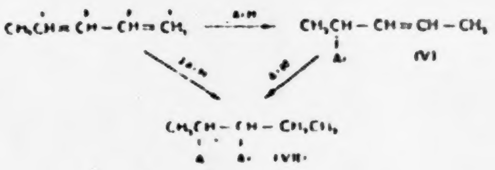
ALKENYLATION OF ANISOLE WITH PIPERYLENE

E. A. Vdovtsova and S. V. Zavgorodny

(Presented by Academician A. V. Topchiev, November 15, 1956)

The alkylation of an aromatic nucleus with dienic hydrocarbons is a field which has been little studied, notwithstanding the availability of the starting materials. Alkylation with butadiene is described in the majority of the available papers and patents [1]. The condensation of piperylene with toluene in the presence of $BF_3 \cdot H_3PO_4$ is reported in only one of the American patents [2]. We might also mention the use of piperylene in the synthesis of 4,7,8-trimethyl-2-ethyl-5-hydroxychroman [3].

We undertook a systematic investigation of the alkylation of the aromatic nucleus with piperylene – which is a by-product in the production of synthetic rubber by the Lebedev process – in order to clarify the reactivity of piperylene as a difunctional compound. Since piperylene contains two equivalent functional groups, it can react with an aromatic compound according to the general scheme [4]:



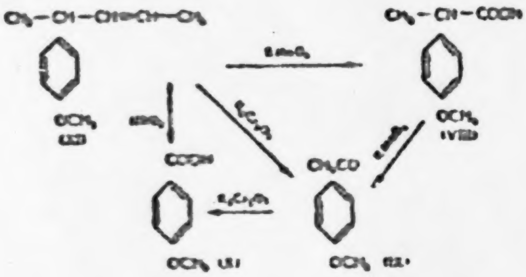
the reaction in stages being the more probable route. For the product containing a double bond, 6 isomers are theoretically possible:

$CH_3CH=CH-CH(Ar)CH_3$ (I)
$CH_3CH=CH-CH_2CH_2Ar$ (II)
$CH_3CH(Ar)CH_2CH=CH_2$ (III)
$CH_3CH_2CH(Ar)CH=CH_2$ (IV)
$CH_3(Ar)CH-CH=CH-CH_3$ (V)
$CH_3CH_2CH=CH-CH_2Ar$ (VI)

As seen, the products of the addition of one molecule of the aromatic compound to piperylene in the 1,2-position (I) and in the 1,4-position (V) have the same structure. As a dienic hydrocarbon, piperylene must react during alkylation so as to produce more rapidly the product of the addition in the 1,4-position (V), in conformity with the distribution of electron density in the molecule [5]. However, 1,4-addition of the aromatic compound in contradiction to Markownikoff's rule (the phenyl radical going to the primary carbon atom) is described in the literature. With substituted benzenes, a different orientation of the pentenyl group is also possible, and among the high boiling products, in addition to products of the diarylpentane (VII) series, can be found polypentenyl benzenes [6]. Thus, a complex mixture of substances may be expected as a result of the reaction.

In the present work, using anisole as the aromatic compound, alkenylation of the aromatic nucleus with piperylene was carried out with yields of pentenylanisoles of 56-92 % of theoretical. Anisole was selected as

Proof of structure of the pentenylanisoles was carried out by oxidation at the double bond of the products obtained with boron trifluoride etherate. Oxidation with $KMnO_4$ in acetone solution gave good yields of p-methoxyhydratropic acid (VIII) and p-methoxyacetophenone (IX), according to:



Oxidation with chromic acid mixture gave a mixture of p-methoxyacetophenone and anisic acid (X). Anisic acid was also obtained by oxidation with 25% nitric acid. The formation of p-methoxyacetophenone undoubtedly indicates that the location of the anisole radical is at the second carbon atom, and the formation of p-methoxyhydratropic acid indicates location at the α-position to the double bond. On this basis, it can be concluded that the pentenylanisole obtained in the presence of $BF_3 \cdot O(C_2H_5)_2$ is mainly 4-(p-methoxyphenyl)-2-pentene (XI), to which reference is made in the literature as an intermediate in the synthesis of 2,3-bis(p-methoxyphenyl)pentane [8], and, consequently, the addition of anisole to piperylene proceeds in conformity with its polarity – (I) or (V).

The products obtained by alkylation in the presence of BF_3, H_3PO_4, and $BF_3 \cdot H_3PO_4$ apparently also consist mainly of 4-(p-methoxyphenyl)-2-pentene. Evidence of this is given by the closeness of the physical constants and by the fact that further reaction of pentenylanisole with anisole forms 2,3-bis(p-methoxyphenyl)pentane, both during the course of this reaction (with BF_3) and when the synthesis is carried out in two stages.

EXPERIMENTAL

The alkylation was carried out in the usual way, as indicated in the theoretical part. Piperylene with a b.p. of 41-42.5°, n_D^{20} 1.4245, d_4^{20} 0.6795, was used. Two main fractions were separated in the fractionation of the pentenylanisoles obtained in the experiments with $BF_3 \cdot O(C_2H_5)_2$.

1st fraction: b.p. 86.5-87.0° at 1 mm, n_D^{20} 1.5178, d_4^{20} 0.9513, MR 56.12, calc. 55.19.

Found %: C 81.58, 81.40; H 8.91, 9.05. $C_{12}H_{16}O$. Calculated %: C 81.77; H 9.16.

2nd fraction: b.p. 88-88.2° at 1.5 mm, n_D^{20} 1.5182, d_4^{20} 0.9513, MR 56.16, calc. 55.19.

Found %: C 81.61, 81.87; H 9.40, 9.56. $C_{12}H_{16}O$. Calculated %: C 81.77; H 9.16.

Both fractions were colorless, highly mobile liquids with a unique odor, and gave the same products on oxidation with $KMnO_4$.

Oxidation of pentenylanisol. a) Oxidation of 5.23 g (0.03 mole) of Fraction 1 dissolved in 125 ml of acetone and 10 ml of water with potassium permanganate gave 2.03 g (42.3% of theoretical) of p-methoxyhydratropic acid [9], m. p. 46-47° (from a mixture of ether and petroleum ether). Distillation of the oil (2.05 g) liberated from the neutral portion gave 1.04 g of a fraction having b.p. 100-130° at 3-4 mm, n_D^{20} 1.5353, and 0.9 g of a fraction having b.p. 130-160° at 3-4 mm, n_D^{20} 1.5364. The 2,4-dinitrophenylhydrazones obtained from these fractions melted, respectively, at 219-220° and 218-219° (from xylene), which correspond to the m. p. of the 2,4-dinitrophenylhydrazone of p-methoxyphenylacetophenone [10]. A mixed sample with the 2,4-dinitrophenylhydrazone of p-methoxyacetophenone, prepared from anisole and acetic anhydride [11], showed no depression of the melting point. The yield of p-methoxyacetophenone was 44.3% of theoretical.

b) Oxidation of Fraction 2 under the same conditions, but in dry acetone, gave 1.83 g (38.3%) of p-methoxyhydratropic acid, m.p. 55-57° (from a mixture of ether and petroleum ether), and 2.03 g (48.6%) of p-methoxyacetophenone, the 2,4-dinitrophenylhydrazone of which melted at 210-213° (from xylene). A mixture with a known sample melted without depression of the melting point.

c) Oxidation of 1.76 g (0.01 mole) of Fraction 1 with 8.9 g of $K_2Cr_2O_7$, 33.2 ml of water, and 9.6 ml of concentrated H_2SO_4 by heating for 3 hours gave 0.7 g (46.6%) of p-methoxyacetophenone; m.p. 2,4-dinitrophenylhydrazone 211-212°; a mixture with a known sample melted at 214-215°. A negligible amount of anisic acid, m.p. 182° (literature data, m.p. 184° [9]), was isolated from the acid portion.

d) Oxidation of 1 g of Fraction 1 with 75 ml of 25% HNO_3 gave anisic acid, m.p. 182-184° (after distillation and repeated crystallization from water and alcohol).

Alkylation of anisole with pentenylanisole in the presence of $BF_3 \cdot H_3PO_4$. From 19.08 g (0.1 mole) of pentenylanisole, prepared with H_3PO_4, 23.3 g (0.22 mole) of anisole, and 3.58 g (0.02 mole) of $BF_3 \cdot H_3PO_4$, after heating on a water bath with stirring for 2 hours, was obtained 10.25 g (33.4%) of dianisylpentane fraction, b.p. 190-207° at 8 mm, d_4^{20} 1.0590, n_D^{20} 1.5610, MR 86.76, calc. 86.03. Upon the addition of absolute alcohol and freezing, the substance almost completely crystallized, m.p. 105-107.0° (from alcohol). Literature data [8] for 2,3-bis(p-methoxyphenyl)-pentane, m.p. 106-108°.

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SYNTHESIS OF ALIPHATIC DIALKYLAMINO ALCOHOLS FROM DERIVATIVES OF THIOPHENE

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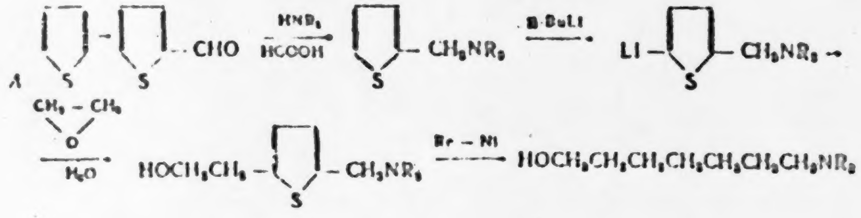
(Presented by Academician A. A. Balandin, November 27, 1956)

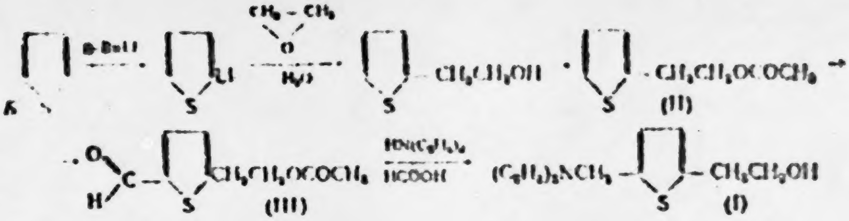
In the light of the data we obtained during a study of the reductive desulfurization of tertiary amines of the thiophene series [1], it was of interest to investigate the possibility of preparing by an analogous route amino alcohols, which, as is well known, are important fragments in the synthesis of physiologically active substances, particularly those with anesthetic, antispasmodic, or hypotensive natures. In this connection, it should be noted that in spite of the very broad range of application of the amino alcohols, methods for their preparation are limited in certain cases by the composition of the initial natural substances, and in other cases by the very principles on which the synthesis is based.

The method developed by us for the preparation of dialkylamino alcohols is illustrated by the following scheme:



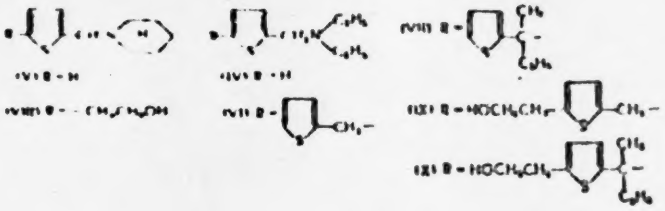
β-Hydroxyethylation of tertiary amines can be carried out by the action of ethylene oxide on the appropriate organolithium compound [2]. The number of methylene units separating the amino group from the hydroxyl group is seven when thiophene is used, but when dithienylmethane is used as the starting material the number increased to twelve. Moreover, there is the possibility of changing the degree of branching of the chain by starting with dithienylmethanes having various alkyl radicals substituted on the methylene group.

The question of the structure of the organolithium compounds formed by the action of butyllithium on tertiary amines of the thiophene series and, consequently, of the structure of the amino alcohols obtained from them could not be considered unequivocally decided a priori, since, in agreement with the views of Gilman [3], coordination of the alkyllithium could be visualized as occurring both at the sulfur atom and at the nitrogen atom. In this connection, we carried out the synthesis of one of the amino alcohols prepared by us, 5-diethylaminomethyl-2-(β-hydroxyethyl)thiophene (I), by a route which had to lead to the formation of only the amino alcohol of structure (I):

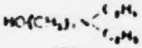


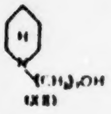
On comparison of this amino alcohol (I) with the amino alcohol of the same composition but prepared by Scheme A, it was clear that they were identical. Thus, it can be considered as proved that the reaction forming organolithium compounds from tertiary amines of the thiophene series proceeds according to Scheme A, and that the amino alcohols formed from them actually have the structure indicated in Scheme A.

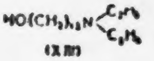
Developing the work in the indicated direction, from amines of the thiophene series (V, IV, VI, VII), of which VI was prepared for the first time, we synthesized by the method indicated aobve the thiophene amino alcohols I, VIII, IX, X:

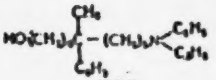


Reductive desulfurization gave the corresponding aliphatic dialkylamino alcohols:


(XI)


(XII)


(XIII)


(XIV)

EXPERIMENTAL

β-Hydroxyethylthiophene acetate [β-thienylethyl acetate] (II). To a solution of 17.8 g (0.14 mole) of β-hydroxyethylthiophene and 22 g (0.28 mole) of dry pyridine in 60 ml of dry benzene was added dropwise and with stirring 13.2 g (0.17 mole) of acetyl chloride. The mixture was treated with 100 ml of ice water, and the benzene layer separated; the aqueous layer was extracted with benzene. The benzene solution was washed with a solution of sodium bicarbonate. After distillation of the solvent, further distillation gave 18.0 g (75% of theoretical) of acetate II with a b.p. of 115-117°/16 mm; n_D^{20} 1.5088; d_4^{20} 1.1303; Found MR_D 44.96; calculated MR_D 44.81.

Found %: C 56.59, 56.30; H 5.86, 5.88; S 18.74, 18.72. $C_8H_{10}SO_2$. Calculated %: C 56.44; H 5.92; S 18.84.

5-(β-Acetoxyethyl)-2-thiophenecarboxaldehyde (III). Acetate II was formylated by the method of Weston and Michaels [4]. From 19.83 g (0.1 mole) of II, 12.2 g (0.09 mole) of N-methylformanilide, and 13.9 g (0.09 mole) of phosphorus oxychloride was obtained 10.7 g (54.5% of theoretical) of acetate III with a b.p. of 173-1[illegible]°/15 mm; n_D^{20} 1.5511; d_4^{20} 1.2142.

Found %: [illegible].16, 54.95, H 5.28, 5.29; S 15.83, 16.17. $C_9H_{10}SO_3$. Calculated %: C 54.52; H 5.08; S 16.17.

The 2,4-dinitrophenylhydrazone melted at 200-201°.

Found %: N 14.61, 14.94. $C_{15}H_{14}SN_4O_6$. Calculated %: N 14.80.

5-Diethylaminomethyl-2-(β-hydroxyethyl)thiophene (I). a) From 7 g (0.35 mole) of III, 4.25 g (0.100 mole) of 96% formic acid, and 5.17 g (0.07 mole) of diethyl amine by the method of Smith and Cavallito [3], which has been used previously in our laboratory [1], was obtained 1.7 g of a substance boiling at 162-165°/15 mm; n_D^{20} 1.5292. Naphthylurethan of I, m.p. 65° (from heptane).

Found %: C 69.35, 69.51; H 6.93, 6.76; S 7.91. $C_{22}H_{26}SN_2O_2$. Calculated %: C 69.08; H 6.85; S 8.38.

b) Hydroxyethylation of 14.2 g (0.08 mole) of diethyl-2-thenylamine (IV) [1] was carried out under the conditions described in reference [2]. The mixture was hydrolyzed, the ether layer separated, and the water layer extracted with ether. After separation of the solvent, distillation of the residue gave 8.1 g of amino alcohol I with a b.p. of 148-150°/7 mm; n_D^{20} 1.5310; d_4^{20} 1.0543; Found MR_D 62.81; calculated MR_D 62.59

Found %: C 61.85, 61.98; H 9.20, 9.11; S 14.87, 14.69. $C_{11}H_{19}SNO$. Calculated %: C 61.92; H 8.98; S 15.03.

Naphthylurethan, m.p. 63-64°. A mixed sample melted without depression of the melting point.

Found %: N 7.09. $C_{22}H_{26}SN_2O_2$. Calculated %: N 7.32.

Amines V and VI were prepared by the method described by us previously [1,5].

N-(2-thenyl)piperidine (V). From 22.4 g (0.2 mole) of thiophene carboxaldehyde, 24 g (0.5 mole) of 90% formic acid, and 34 g (0.4 mole) of piperidine was obtained 23.3 g (64.5% of theoretical) of V; b.p. 102-106°/mm, n_D^{20} 1.5390; d_4^{20} 1.0443; Found MR_D 54.38; calculated MR_D 54.25. Campbell and Kaeding reported a b.p. of 130.5°/29 mm; n_D^{23} 1.5373.

Found %: C 66.55, 66.36; H 8.27, 8.34. $C_{10}H_{15}SN$. Calculated %: C 66.25; H 8.34.

Methiodide, m.p. 160° (from abs. alcohol). Campbell and Kaeding reported m.p. 83° for the methiodide of V. This figure is undoubtedly in error, since the methiodide of a sample of V synthesized by us by the method of Campbell and Kaeding from chloromethylthiophene also melted at 160°, and a mixture with the above methiodide melted without depression of the melting point.

Found %: N 4.47, 4.26. $C_{11}H_{18}SNI$. Calculated %: N 4.33.

5-Diethylaminomethyldi-2-thienylmethane (VI). From 35 g (0.17 mole) of 5-(2-thenyl)thiophene-2-carboxaldehyde [7], 20.7 g (0.40 mole) of 90% formic acid, and 25.2 g (0.35 mole) of diethylamine was obtained 30.35 g (68% of theoretical) of an amine with a b.p. of 176-177.5°/7 mm; n_D^{20} 1.5641; d_4^{20} 1.0887; Found MR_D 79.30; Calculated MR_D 79.05.

Found %: C 63.23, 63.19; H 7.17, 7.24; S 24.23, 24.43. $C_{14}H_{19}S_2N$. Calculated %: C 63.35; H 7.21; S 24.16.

Methiodide, m.p. 151.5-152.5 (from absolute alcohol).

Found %: N 3.20, 3.28. $C_{13}H_{22}S_2NI$. Calculated %: N 3.44.

5-(1-Piperidinomethyl)-2-(β-hydroxyethyl)thiophene (VIII) was prepared similarly to I. From 14 g (0.08 mole) of V, 5.2 g (0.08 mole) of butyllithium, and 5.3 g (0.12 mole) of ethylene oxide was obtained 8.8 g of an amino alcohol with a b.p. of 173-177°/8 mm; n_D^{20} 1.5520; d_4^{20} 1.1040; Found MR_D 65.22; Calculated MR_D 65.01.

Found %: C 63.64, 63.93; H 8.64, 8.43; S 14.05, 14.19. $C_{12}H_{19}SNO$. Calculated %: C 63.95; H 8.50; S 14.23.

Methiodide, m.p. 92-93° (from absolute alcohol).

Found %: N 3.99, 4.11. $C_{13}H_{22}SNOI$. Calculated %: N 3.97.

5'-Diethylaminomethyl-5-(β-hydroxyethyl)-2,2'-dithienylmethane (IX) was prepared similarly to I. From 39.5 g (0.15 mole) of VI, 9.6 g (0.15 mole) of butyllithium, and 10 g (0.22 mole) of ethylene oxide was obtained 16.7 g (36.5% of theoretical) of IX; b.p. 198-204°/4 mm; m.p. 48-49° (from petroleum ether).

Found %: C 62.17, 62.26; H 7.52, 7.54; S 20.58, 20.95. $C_{16}H_{23}S_2NO$. Calculated %: C 62.09; H 7.49; S 20.72.

The hydrochloride of the p-nitrobenzoate of IX was prepared by saturating an ethereal solution of the p-nitrobenzoate of IX with dry hydrogen chloride [8]; m.p. 163.5-164° (from absolute alcohol).

Found %: C 55.37, 55.59; H 5.37, 5.65. $C_{23}H_{27}S_2N_2O_4Cl$. Calculated %: C 55.80; H 5.50.

2-(5'-Diethylaminomethyl-2'-thienyl)-2-(5-β-hydroxyethyl-2-thienyl)butane (X) was prepared similarly to I. From 33.75 g (0.11 mole) of VII [1], 7.1 g (0.11 mole) of butyllithium, and 7.1 g (0.16 mole) of ethylene oxide was obtained 26.1 g of X with a b.p. of 233-236°/7 mm; 213-216°/4 mm n_D^{20} 1.5639; d_4^{20} 1.1045; Found MR_D 103.52; Calculated MR_D 103.66.

Found %: C 64.77, 64.70; H 8.16, 8.29; S 18.13, 18.17. $C_{19}H_{29}S_2NO$. Calculated %: C 65.09; H 8.34; S 18.29.

The reductive desulfurization of the amino alcohols of the thiophene series was carried out by the method previously described by us [1] using skeletal Ni catalyst prepared by the method of Adkins [9].

1-Diethylamino-7-heptanol (XI). From 35.4 g of I, after a 30-minute heating with Raney Ni, was obtained 13.8 g (44.5% of theoretical) of a substance with a b.p. of 130-132°/9 mm. By a second distillation was obtained 12.5 g of (XI) with a b.p. of 129.5-130°/9 mm; n_D^{19} 1.4569. Literature data: b.p. 132°/9.5 mm; n_D^{19} 1.4561 [10]; b.p. 139-141°/25 mm [11].

Found %: C 70.21, 70.15; H 13.32, 13.16. $C_{11}H_{25}NO$. Calculated %: C 70.50; H 13.47.

The hydrochloride of (7-chloroheptyl)diethylamine (XV) melted at 85° (cf. [11]).

Found %: N 5.66, 5.86. $C_{11}H_{25}NCl_2$. Calculated %: N 5.78.

1-Piperidino-7-heptanol (XII). From 9 g of VIII, after a 30 minute heating with Raney Ni, was obtained 4 g (50% of theoretical) of an amino alcohol with a b.p. of 147-150°/7 mm. A second distillation gave 2.4 g of XII with a b.p. of 144-147°/7 mm; n_D^{20} 1.4771; d_4^{20} 0.9253; Found MR_D 60.88; Calculated MR_D 60.88. Hydrochloride of N-(7-chloroheptyl)piperidine, m.p. 148-148.5° (reprecipitated from alcohol by ether).

Found %: C 56.15, 56.45; H 10.07, 10.00; Cl 27.43. $C_{12}H_{25}NCl_2$. Calculated %: C 56.68; H 9.91; Cl 27.89.

1-Diethylamino-12-dodecanol (XIII). From 10 g amino alcohol IX, after a 30-minute heating with Raney Ni, was obtained 4 g (43% of theoretical) of a substance with a b.p. of 140-178°/7 mm. A second distillation gave 2 g of XIII with a b.p. of 175-178°/7 mm; n_D^{20} 1.4611; d_4^{20} 0.8891; Found MR_D 81.30; Calculated MR_D 81.55.

Found %: C 74.64, 74.58; H 13.63, 13.61. $C_{16}H_{35}NO$. Calculated %: C 74.64; H 13.70.

1-Diethylamino-6-methyl-6-ethyl-12-dodecanol (XIV). From 6.5 g of X, after a 45-minute heating with Raney Ni, was obtained 2 g (theoretical) of a substance with a b.p. of 170-193°/7 mm. A second distillation gave 1.2 g of XIV with a b.p. of 190-192°/7 mm; n_D^{20} 1.4650; d_4^{20} 0.8862; Found MR_D 95.69; Calculated MR_D 95.41.

Found %: C 75.97, 76.28; H 13.69, 13.71. $C_{19}H_{41}NO$. Calculated %: C 76.18; H 13.80.

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* Original Russian pagination. See C. B. translation.

PAGE 287 MISNUMBERED, SHOULD READ
PAGE 267.

CHLOROSULFONATION OF METHANE WITH SULFUR DIOXIDE AND CHLORINE

G. V. Gryaznov, Academician A. V. Topchiev and G. M. Tsiguro

At the present time there is no known method for the production of methanesulfonyl chloride by the direct chlorosulfonation of methane. This compound is usually prepared from salts of methanesulfonic acid by the action of phosphorus pentachloride [1] or from free methanesulfonic acid and thionyl chloride [2]; in the latter case, up to 80% methanesulfonic anhydride is simultaneously formed [3]. The best results in the preparation of methanesulfonyl chloride are obtained by chlorination of methylisothiourea [4].

The chlorosulfonation reaction proceeds difficultly with ethane and still more difficultly with methane. We carried out experiments on the photochemical chlorosulfonation of methane in a quartz apparatus. During the course of the experiments, observations were carried out on the composition of the reaction mixture in the gaseous and vapor state. Irradiation of the gaseous reaction mixture was carried out with ultraviolet light having a wavelength of 3650 A or with x-rays ($\lambda_{ef} = 1,6$ A).

Appreciable amounts of methanesulfonyl chloride were not formed in the gas phase under the influence of ultraviolet light or of powerful x-ray irradiation (intensity of the beam at the tube window was $12,6 \cdot 10^{13}$ ev/sq. cm²·sec or ~ 2000 r/second). The main reaction products under these conditions were chloro derivatives of methane and sulfuryl chloride, which were isolated in very small amounts.

We feel that photochemical chlorosulfonation of aliphatic hydrocarbons can proceed not only by a chain mechanism [5], but, as shown by our experiments, the formation of alkane sulfonic acids (as intermediate compounds) can also take place.

Under the influence of activating radiation, reaction of the aliphatic hydrocarbon with an activated sulfur dioxide molecule proceeds with the formation of an alkanesulfinic acid

$$RH + SO_2^{*} \xrightarrow{h\nu} RSO_2H$$

and it is then oxidized by chlorine to form the sulfonyl chloride and hydrogen chloride

$$RSO_2H + Cl_2 \rightarrow RSO_2Cl + HCl.$$

During the chlorosulfonation of methane, the most difficult stage is the formation of methanesulfinic acid, which is formed from methane and sulfur dioxide with a yield which is ten times less than for other hydrocarbons. The quantum yield of methanesulfinic acid attains a value of only 0.008, while in the formation of butanesulfinic acid this value is about 0,23 [6]. The very low content of methanesulfonyl chloride in the products of the photochemical chlorosulfonation of methane with gaseous sulfur dioxide and chlorine is evidently due to the low specific role of the formation of methanesulfinic acid in comparison with the simultaneously occurring photochemical chlorination of methane.

For a more successful direct synthesis of methanesulfonyl chloride, it is necessary to carry out the chlorosulfonation of methane under conditions permitting a higher degree of dissociation of methane with the formation of methyl radicals than is observed during the action of ultraviolet irradiation.

For confirmation of this conclusion, we carried out special experiments on the chlorosulfonation of methane with gaseous sulfur dioxide and chlorine in a flow system in the field of a high-frequency electric discharge (calculated wavelength 357.6 m). The generator of the high-frequency attenuated vibrations was a "Tesla" transformer with an output of 200 watts at 1,000,000 volts. This transformer was fed with a 1-kw oil transformer with a 10,000 volt output.

The apparatus used for these experiments was a vertical glass tube, along the axis of which was a second glass tube of 2-mm diameter which was filled with mercury and which served as the electrode to which was fed the high voltage. The external grounded electrode was a wire spiral which was submerged in a conductor in contact with the reaction tube.

Under the conditions described, the yield of methanesulfonyl chloride reached 2-3%, calculated on the methane. The formation of methanesulfonyl chloride was demonstrated by the preparation from it of the meta naphthylsulfamide.

The initial reaction gases were fed to the reactor in equimolar amounts. The feed rate of the gases was varied in the different experiments so that the residence time of the reaction mixture in the field of the discharge varied from 0.8 to 4.4 minutes.

During the chlorosulfonation of methane, sulfur was deposited on the wall of the reactor in a considerable amount. Besides methanesulfonyl chloride, an insignificant amount of methionyl chloride ($CH_2(SO_2Cl_2)_2$) and rather large amounts of mono- and tri- chloromethanesulfonyl chloride ($ClCH_2SO_2Cl$, Cl_3CSO_2Cl), methylene chloride, chloroform, carbon tetrachloride, sulfuryl chloride, and carbon disulfide were observed in the liquid reaction products.

The formation, under these conditions, of methanesulfonyl chloride can be represented as a chain process, initiated, chiefly, by methyl radicals formed in the process of the dissociation of methane molecules, which is excited by the high-frequency electric discharge:

$$CH_4 \rightsquigarrow CH_4^{\circ} \rightarrow CH_3^{\bullet} + H^{\bullet} \qquad (I)$$

and also as a result of the reaction of methane molecules with chlorine atoms:

$$CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl.$$

The methyl radicals react with molecules of sulfur dioxide with the formation of methanesulfinic radicals

$$CH_3^{\bullet} + SO_2 \rightarrow CH_3SO_2^{\bullet},$$

which, reacting with chlorine, given methanesulfonyl chloride

$$CH_3SO_2^{\bullet} + Cl_2 \rightarrow CH_3SO_2Cl + Cl^{\bullet}.$$

The preparation of methanesulfonyl chloride in the field of a high-frequency electric discharge confirmed our supposition that chlorosulfonation of methane with gaseous sulfur dioxide and chlorine can proceed with appreciable yields only under those conditions where the method of carrying out the experiment provides for the formation of a relatively large excess of methyl radicals in comparison with chlorine atoms. Under the conditions of our experiments, as a consequence of the insufficient formation of methyl radicals according to Scheme (I) and also owing to the comparatively high concentration of molecular and atomic chlorine in the reaction mixture, the chain process of the chlorosulfonation of methane was not markedly developed, apparently owing to breaking of the reaction chain by consumption of the radicals in the processes:

$$SO_2 + Cl^{\bullet} \rightarrow {}^{\bullet}SO_2Cl;$$
$$CH_3^{\bullet} + {}^{\bullet}SO_2Cl \rightarrow CH_3SO_2Cl;$$
$${}^{\bullet}SO_2Cl + Cl^{\bullet} \rightarrow SO_2Cl_2.$$

The specific role of the chlorosulfonation of methane is decreased, moreover, by various side reactions (among them the methane chlorination chain reaction) resulting in the liberation of the compounds indicated above.

Thus, two mechanisms of the chlorosulfonation of saturated aliphatic hydrocarbons can occur:

1. Photochemical chlorosulfonation proceeds through a stage of the formation of a sulfinic acid, and it is oxidized by chlorine to the sulfonyl chloride.

2. Chlorosulfonation in the field of an electric discharge proceeds through a stage of the formation of radicals, and has a chain mechanism.

The possibility, in principle, of the preparation of methanesulfonyl chloride by the direct chlorosulfonation of methane with gaseous sulfur dioxide and chlorine was experimentally demonstrated.

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SYNTHESIS OF C-C DERIVATIVES OF l-ARABINOSE

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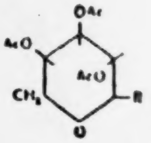
(Presented by Academician A. I. Oparin, November 21, 1956)

In previously published work [1-3], we described the preparation of some carbon-carbon substituted monoses (glucose, galactose, xylose) by organomagnesium synthesis. This route has still not been used for the synthesis of C-C derivatives of l-arabinose, which enters into the composition of many natural substances.

By reacting β-chlorotriacetyl-l-arabinose with the appropriate Grignard reagent, we synthesized C-C derivatives of this carbohydrate containing the following radicals: phenyl, anisyl, naphthyl, phenetyl, o-tolyl, p-tolyl, thienyl, and butyl. The general formula for these compounds is:



Chlorination, bromination, and iodination of anisyl and phenetylarabinose gave the corresponding halogen derivatives.

EXPERIMENTAL

α-Tetracetyl-l-arabinose was prepared by acetylation of l-arabinose with acetic anhydride in the presence of sodium acetate [4]. For the synthesis of β-chlorotriacetyl-l-arabinose, 20 g (0.063 mole) of the tetracetylarabinose was dissolved in 60 ml of chloroform, and 13.1 g (0.063 mole) of phosphorus pentachloride and 5 g (0.017 mole) of aluminum chloride were added. The mixture was heated in a flask fitted with a reflux condenser on a boiling water bath. The solution was poured into ice water, and the chloroform layer was separated, washed with a solution of sodium bicarbonate and with water, dried over sodium sulfate, and decolorized with activated carbon. The transparent solution was diluted twofold with normal hexane, and the solvent was slowly evaporated. The product was a pure crystalline material with m.p. 150-152°. The yield was 15-16 g (85% of theoretical).

Phenyltriacetyl-l-arabinose. Then ethereal solution of phenylmagnesium bromide, prepared from 4.08 g (0.17 mole) of magnesium and 26.7 g (0.17 mole) of bromobenzene, was added portion-wise 5 g of chlorotriacetyl-l-arabinose. The mixture was heated on a water bath for 4 hours, poured into water, and decomposed with acetic acid. The water layer was evaporated to dryness and acetylated; the reaction mixture was poured into water, extracted with ether, and the ether solution was washed with water and dried. On distillation of the ether there was obtained 2.7 g of a light yellow syrup, which was dissolved in a small amount of butanol. On cooling, 1.5 g of phenyltriacetyl-l-arabinose was obtained. An additional 0.8 g of the material was separated by evaporation of the mother liquor. The total yield was 2.3 g (42% of theoretical). M.p. 91-92°. The substance is described here for the first time.

Found %: C 60.85; H 6.06. $C_{17}H_{20}O_7$. Calculated %: C 60.71; H 5.95.

o-Tolyltriacetyl-l-arabinose, To an ethereal solution of Grignard reagent, prepared from 3.93 g (0.16 mole) of magnesium and 27.4 g (0.16 mole) of o-bromotoluene, was added 5 g of chlorotriacetyl-l-arabinose. Further treatment was carried out by the preceding method. Recrystallization from butanol gave 1.9 g (33% of theoretical) of o-tolyltriacetyl-l-arabinose in the form of a white crystalline powder with m.p. 99-100°. The substance is described here for the first time.

Found %: C 61.62; H 6.24. $C_{18}H_{22}O_7$. Calculated %: C 61.72; H 6.28.

p-Tolyltriacetyl-l-arabinose. The compound was prepared by the preceding method starting with 3.5 g (0.012 mole) of chloroacetylarabinose, 20.5 g (0.12 mole) of p-bromotoluene, and 2.8 g (0.12 mole) of magnesium. Recrystallization from butanol gave 2 g (50% of theoretical) of p-tolyltriacetyl-l-arabinose in the form of snow-white needles with m.p. 102-103°. The substance is described here for the first time.

Found %: C 61.66; H 6.23. $C_{18}H_{22}O_7$. Calculated %: C 61.71; H 6.28.

Naphthyltriacetyl-l-arabinose, An ethereal solution of 3.9 g (0.013 mole) of chlorotriacetyl-l-arabinose was gradually added to a Grignard reagent prepared from 29 g (0.14 mole) of α-bromonaphthalene and 3.38 g (0.14 mole) of magnesium. Further treatment was carried out by the usual method. Recrystallization from butanol gave 0.8 g (15% of theoretical) of white, crystalline naphthyltriacetyl-l-arabinose with m.p. 137-138°. The substance is described here for the first time.

Found %: C 65.55; H 5.45. $C_{21}H_{22}O_7$. Calculated %: C 65.28; H 5.69.

Thienyltriacetyl-l-arabinose, 25.2 g (0.12 mole) of 2-iodothiophene and 2.88 g (0.12 mole) of magnesium were used for the synthesis of the Grignard reagent. 3.7 g (0.011 mole) of chlorotriacetyl-l-arabinose was added to the solution of the Grignard reagent. The usual treatment and recrystallization from isopropyl alcohol gave 0.8 g (20% of theoretical) of white, crystalline thienyltriacetyl-l-arabinose with m.p. 96-97°. The substance is described here for the first time.

Found %: C 52.34; H 5.48. $C_{15}H_{18}O_7S$. Calculated %: C 52.47; H 5.54.

Anisyltriacetyl-l-arabinose. An ethereal solution of 5 g (0.016 mole) of chlorotriacetyl-l-arabinose was added to an ethereal solution of Grignard reagent prepared from 31.8 g (0.16 mole) of p-bromoanisole and 4.08 g (0.16 mole) of magnesium. The usual treatment and recrystallization from butanol gave 2.5 g (41% of theoretical) of anisyltriacetyl-l-arabinose in the form of lustrous, cream-colored needles with m.p. 153-154°. The substance is described here for the first time.

Found %: C 59.14; H 5.96. $C_{18}H_{22}O_8$. Calculated %: C 59.01; H 6.01.

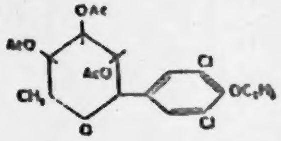
Phenetyltriacetyl-l-arabinose, An ethereal solution of 7.5 g (0.026 mole) of chlorotriacetyl-l-arabinose was added to an ethereal solution of Grignard reagent prepared from 49 g (0.24 mole) of p-bromophenetole and 5.76 g (0.24 mole) of magnesium. The usual treatment and recrystallization from butanol gave 3.6 g (36% of theoretical) of phenetyltriacetyl-l-arabinose in the form of needles with m.p. 126-127°. The substance is described here for the first time.

Found %: C 59.93; H 6.25. $C_{19}H_{24}O_8$. Calculated %: C 60.00; H 6.32.

Chloroanisyltriacetyl-l-arabinose, 0.5 g of anisyltriacetyl-l-arabinose was dissolved in 10 ml of carbon tetrachloride saturated with chlorine. After an hour, the solution was poured into water; the organic layer was separated, washed with a solution of sodium bicarbonate, and dried with anhydrous sodium sulfate, after which the solvent was distilled. The sirupy residue was dissolved in a small amount of hot isopropyl alcohol. On cooling, 0.45 g of white, crystalline chloroanisyltriacetyl-l-arabinose, m. p. 97-98°, was obtained. The substance is described here for the first time.

Found %: C 53.64; H 5.41; Cl 8.77. $C_{18}H_{21}O_8Cl$. Calculated %: C 53.79; H 5.48; Cl 8.84.

Dichlorophenetyltriacetyl-l-arabinose. 0.5 g of p-phenetyltriacetyl-l-arabinose was chlorinated under the same conditions used in the preceding experiment. This gave 0.65 g of a sirup which we were unable to crystallize. The product contained 15.41% chlorine, which corresponds to the chlorine content of dichlorophenetyltriacetyl-l-arabinose (calculated, 15.81% chlorine). The obvious structure of the product, considering the orienting effect of the ethoxy group, is the following:



Bromoanisyltriacetyl-l-arabinose. 0.9 g of p-anisyltriacetyl-l-arabinose was dissolved in a mixture of 26 ml of glacial acetic acid and 3.5 g of bromine. After an hour, the solution was poured into water and extracted with ether; the ether layer was washed with water and a solution of sodium bicarbonate and then dried, after which the ether was distilled. Recrystallization from butanol gave 0.9 g of bromoanisyltriacetyl-l-arabinose in the form of colorless needles with m.p. 129-130°. The substance is described here for the first time.

Found %: C 48.36; H 4.85; Br 18.03. $C_{18}H_{21}O_8Br$. Calculated %: C 48.43; H 4.93; Br 17.97.

Dibromophenetyltriacetyl-l-arabinose. In a similar manner, bromination of 0.9 g of phenetyltriacetyl-l-arabinose gave 0.85 g of an uncrystallizable sirup of the dibromo derivative. The substance contained 30.24% bromine (calculated, 29.75%). The substance is described here for the first time.

Iodination of the anisyl- and phenetyl-substituted arabinoses with iodine chloride gave the iodo derivatives in the form of sirups. Butyltriacetyl-l-arabinose was also obtained in the form of an uncrystallizable sirup in 6.8% yield.

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* Original Russian pagination. See C. B. translation.

CONDITIONS FOR THE FORMATION OF SOLID SOLUTIONS OF ORGANIC SUBSTANCES

A. I. Kitaigorodsky

(Presented by Academician A. N. Nesmeyanov, October 18, 1958)

The attractive forces acting between the molecules from which organic molecules are constructed have an extremely weak directive influence. Therefore, the tendency toward minimum energy finds expression in a tendency toward dense packing [1]. The symmetry class and the dense packing are completely sufficient for an understanding of the structure of an organic crystal. In contrast to this, in metallic and inorganic crystals, interatomic electron bonds can completely suppress symmetry factors and dense packing.

It is precisely for this reason that it is possible to attempt the formulation of rules for the formation of solid solutions of orga[illegible] attempt being unsuccessful for other classes of compounds). Chiefly, substitutional solid so[illegible] in organic crystals. A foreign molecule can replace a molecule of the basic crystal if the molecules of both types are similar in form and dimensions.

Closeness of atomic dimensions is a necessary condition for the formation of substitutional solid solutions in inorganic and metallic crystals. In organic crystals, similarity of form and dimensions of the molecules is necessary and sufficient; however, it is considerably more difficult here to characterize the amount of isomorphism of the molecules.

Analysis of the existing experimental data shows that substance A dissolves in substance B under the following conditions. Let us imagine that one molecule of substance B is removed from a crystal. We now place a molecule of A in the vacant place in the ideal crystal lattice of B. If the substitution can be carried out with approximately the same number of contacts and with retention of the intermolecular radii within permissible limits, then a solid solution is formed by the mixture. The permissible limits of intermolecular radii for H, C, N, and O atoms are, respectively, 1.05-1.35, 1.65-1.85, 1.45-1.65, and 1.30-1.50 A.

We now make a further attempt to establish a correlation between fractional solubility and the dimensions resulting from the mixture of compression and voids.

Solution by addition is possible in organic systems in rare cases. The packing coefficient of organic molecules in a crystal is in the range 0.6 to 0.8 [1]. This means that in organic crystals, small voids are possible with a total volume of the order of 10% of the volume of the molecule.

Thus, additive solid solutions of A in B are formed if the volume of A is approximately 10 times less than that of molecule B. It is understood that not only the volume, but also the form of the voids is important.

Substitutional solid solutions are also possible with unlimited solubility; however, for the formation of such solutions, isomorphism of the molecules is merely required, but is not a sufficient condition.

If molecules A and B are approximately the same in form and dimension, molecule A can replace molecule B in the crystal. During substitution, the symmetry of distribution of molecules in the crystal of B can either remain as before, or it can immediately change discontinuously with the entry of the first molecules of [illegible] B.

The symmetry of distribution of molecules in the crystal of B can remain as before in the following cases: a) with any symmetry of molecule A, if molecule B occupies an asymmetric position* in the crystal; b) with [illegible] asymmetric position or body does not contain an inversion center nor mirror planes of symmetry.

...

nonasymmetric molecules of A or with an equal number of levo and dextro forms of molecules of A, if the molecules of B occupy a nonasymmetric position in the crystal.

The symmetry of the distribution of the molecules in the crystal changes discontinuously on the introduction of the first molecules of A into the solution if the molecule of B occupies an asymmetric position in the crystal and the molecules of A are asymmetric (one of the forms).

Let A be soluble in B and B be soluble in A. With similar forms of the molecules, a continuous series of solid solutions is possible in the following cases: a) if the symmetry of the distribution of molecules in crystals of A and B is the same; b) if the symmetry of distribution of the molecules in crystals of A and B differ, but the symmetry of the distribution of the molecules in crystal of B changes discontinuously with the introduction of molecules of A into the crystal of B. This applies particularlyto the solution of asymmetric molecules in a recemate. A continuous series of solid solutions is impossible if the symmetry of the distribution of molecules in crystals of A and B differ and if, in addition, the molecules of A enter B without changing the symmetry of the distribution of the molecules in the crystal of B, and molecules of B enter A without changing the symmetry of the distribution of the molecules in the crystal of A. In this case, there are two solid phases, and this means a miscibility gap.

Ignoring asymmetric molecules, it is possible to state that the required condition for the formation of solid solutions in all proportions (this relates to all three types of continuous solid solutions) is identical symmetry of the reciprocal distribution of the molecules of the mixed substances, i.e., identical space group numbers of the molecules in the unit cell.

Examples of organic substances in which not only are the molecules very close in form and dimension, but very similar in molecular packing are known. If, with this similarity, there is, nevertheless, a difference in the symmetry of the reciprocal distribution of the molecules, then a continuous series of solid solutions becomes impossible. In any concentration interval there must exist a miscibility gap, or, in other words, a continuous change in concentration in the solid state is possible only through a phase transition.

The closer the molecules of such crystals in form and the more related in packing, the more probable is a miscibility gap. Therefore, it is no wonder that investigators have not noted this gap, and have found continuous series of solid solutions of types I and III where actually there are, respectively, solutions of types IV and V.

An extremely great number of systems have been erroneously described in the literature as continuous solid solutions.

Thus, for example, the following systems have been incorrectly referred to as solid solutions of type I (data from Landolt): anthracene-carbazole; anthracene-phenanthrene; benzene-thiophene; heptadecane-hexadecane; heptadecane-octadecane; biphenyl-3-fluorobiphenyl; dibenzyl-stilbene; dibenzyl-tolane; naphthalene-β-naphthol.

The following have been incorrectly referred to as type III: acridine-anthracene; acridine-phenanthrene; azobenzene-dibenzyl; naphthalene-β-chloronaphthalene; 1,5-dinitronaphthalene-1,8-dinitronaphthalene; 1,5-dinitronaphthalene-1,3,8-trinitronaphthalene; biphenyl-3-fluorobiphenyl.

It is sufficient to note that anthracene, biphenyl, and naphthalene have 2 molecules in a unit cell of C_{2h}^{5} symmetry, which is impossible for substances the molecules of which lack a center of symmetry.

We encountered erroneous structural diagrams during an investigation of the structure of solid solutions of organic substances by x-ray structural analysis. The results of this work, first with respect to the structure of solid solutions of the systems stilbenedibenzyl and phenanthrene-anthracene, will be reported in another place.

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INVESTIGATION OF THE MECHANISM OF THE ALKYLATION OF ALCOHOLS WITH N-TRIMETHYL-α-PHENETYLAMMONIUM IODIDE

Corresponding Member Acad. Sci. USSR D. N. Kursanov and S. V. Vitt

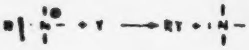
The aim of our work was the investigation of the question of the mechanism of alkylation with ammonium salts containing a substituted benzyl (α-phenetyl) radical.

It is well known that ammonium compounds alkylate alcohols with the formation of ethers. In particular, N-benzyldimethylphenylammonium chloride reacts with alcohols at a temperature of 140-180° forming the benzyl ethers of the alcohols [1]:

$$PhCH_2\overset{\oplus}{N}Me_2Ph + C_5H_{11}OH \longrightarrow PhCH_2OC_5H_{11} + H\overset{\oplus}{N}Me_2Ph$$

Ammonium salts containing a substituted benzyl radical also undergo alkylation [2,3].

It has been established by a number of authors that alkylation with ammonium compounds is a heterolytic substitution reaction [1,3,5,6]:



$$R\,|\cdot\overset{|\,\oplus}{\underset{|}{N}}- + Y \longrightarrow RY + :\overset{|}{\underset{|}{N}}-$$

However, up to the present time there have not been sufficient data for a solution to the problem of the precise manner in which the transfer of the radical from the ammonium nitrogen to the alkylatable substance (for example, an alcohol) proceeds.

Alkylation reactions with ammonium compounds are related to S_N type substitution reactions, which can proceed by two routes:

1. The formation of the new bond proceeds simultaneously with the rupture of the old. Such reactions are called synchronous reactions. Reactions proceeding through an activated complex are characteristic examples of synchronous processes.

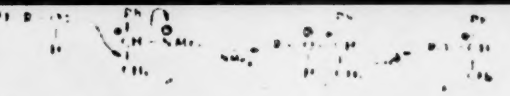
2. The formation of the new bond precedes the complete rupture of the old bond. Free carbonium ions are formed thereby. Such reactions are called asynchronous reactions.

The use of optically active substances permits differentiation between synchronous and asynchronous processes. Synchronous reactions involving an asymmetric center are accompanied by inversion (or retention) of configuration, while asynchronous reactions (proceeding through the intermediate formation of free carbonium ions) are accompanied by complete racemization as a consequence of the planar structure of carbonium ions.

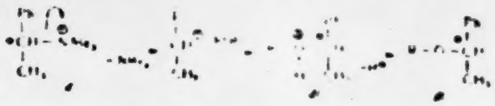
We studied alkylation of methyl, ethyl, and n-butyl alcohols by an optically active d-N-trimethyl-α-phenetylammonium salt.

If the reaction proceeds by a synchronous mechanism, then, on the basis of the above discussion, optical activity must be retained in the reaction products; if the reaction proceeds by an asynchronous mechanism, the reaction products must be void of optical activity:

(A)



(B)



The alkylation reaction was studied in the temperature interval 135-155° (at a temperature below 135°, the alkylation of alcohols by N-trimethyl-α-phenetylammonium iodide proceeds too slowly). The alcohol being alkylated, which was used in excess, served as the solvent. The α-phenetyl alkyl ethers formed in the reactions were investigated polarimetrically.

It was shown that in all of the cases investigated the ethers obtained did not possess optical activity. However, it was still not clear whether racemization occurred during the alkylation reaction or in the original ammonium salt as a result of heating with alcohol at the high temperature. In order to answer this question, we carried out the reaction under conditions such that the d-N-trimethyl-α-phenetylammonium iodide did not react completely. The unreacted N-trimethyl-α-phenetylammonium iodide was subsequently isolated from the reaction mixture by fractional crystallization. It was shown that the salt isolated from the reaction mixture almost completely retained its original optical activity, while the α-phenetyl methyl ether obtained was almost completely devoid of optical activity.

It follows from these data that the alkylation of alcohols by N-trimethyl-α-phenetylammonium salts proceeds through the intermediate formation of an α-phenetyl carbonium ion, i.e., by an asynchronous mechanism (Scheme B).

EXPERIMENTAL

1. d-N-dimethyl-α-phentylamine. A mixture of 156 g of pure d-α-phentylamine l-malate [7], 180 ml of 85% formic acid, and 175 ml of 30% formalin was heated at 95° for 10 hours, 75 ml of concentrated hydrochloric acid was then added, after which the formic acid and water were distilled under vacuum. The residue was dissolved in water, alkalized, and steam distilled. The distillate was extracted with 20 ml of acetic anhydride, alkalized, and extracted with benzene. The product was fractionated. The yield of d-N-dimethyl-α-phenetylamine was 73.2 g (81% of theoretical); n_D^{20} 1.5022 - 1.5024; d_4^{20} 0.9027 - 0.9030; $[\alpha]_D^{20}$ = + 70.8-71.6° (without solvent). *

It has been reported [8] that l-N-dimethyl-α-phenetylamine has $[\alpha]_D^{20}$ - 65.3°.

2. d-N-Trimethyl-α-phenetylammonium iodide was prepared from d-N-dimethyl-α-phenetylamine and methyl iodide by a well-known method from the literature [9]. The material, recrystallized from a mixture of acetone and ether, had a m.p. of 157-157.5°,** $[\alpha]_D^{20}$ = + 12.3° (in H_2O, C = 8.8 %).

3. Reaction of d-N-trimethyl-α-phenetylammonium iodide with methyl alcohol. 0.05 mole of d-N-trimethyl-α-phenetylammonium iodide and 0.2 mole of absolute methyl alcohol were heated in a sealed ampoule for 5 hours at 136 ± 1°.

The contents of the ampoule were treated with 50 ml of absolute, peroxide-free ether. The ammonium salt was quickly suction filtered and washed on the filter with a small amount of ether. The resulting ethereal solution was washed with water, with a 0.5 N solution of sulfuric acid, and again with water, after which it was dried with potassium carbonate. The solvent was distilled in a column. 1.63 g of α-phenetyl methyl ether was isolated, b.p. 68.5-69.5° (20 mm), n_D^{20} 1.4951.

Determination of optical activity showed that this substance was racemic.

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* In a similar manner, optically pure l-N-dimethyl-α-phenetylamine, $[\alpha]_D^{25}$ = -71.2° (without solvent), was obtained by methylation of l-α-phenetyl amine d-tartrate.

** dl-salt, m.p. 147-148°.

From the ether-insoluble ammonium salt mixture (11,5 g) were obtained, by recrystallization from acetone-ether, 2.21 g of tetramethylammonium iodide and 7.51 g of N-trimethyl-α-phenetylammonium iodide which melted at 142.6-143.5°. Determination of the optical activity showed that the unreacted salt had a specific rotation differing only slightly from the specific rotation of the original d-N-trimethyl-α-phenetylammonium iodide ($[\alpha]_D^{20}$ = + 11.5° in place of +12.3° for the original salt).

These data show that the alkylation of methyl alcohol proceeds with the formation of an α-phenetyl carbonium ion.

The results of the experiments on the alkylation of methyl alcohol with N-trimethyl-α-phenetylammonium iodide are presented in Table 1.

TABLE 1

Configuration of Ammonium salt	Reaction temperature °C	Reaction time, hours	n_D^{20}	B.p. °C (mm)	Configuration of the α-phenetyl methyl ether
dl	130	8	1.4930	62—64 (17)	—
dl	155—8	4	1.4949	56—57 (12)	—
d	153—5	4	1.4946	75—78 (32)	dl
d	135—7	5	1.4951	63.5—69.5 (20)	dl

4. Reaction of d-N-trimethyl-α-phenetylammonium iodide with ethyl alcohol. 0,1 mole of d-N-trimethyl-α-phenetylammonium iodide and 0,42 mole of absolute ethyl alcohol were heated in a sealed ampoule for 11 hours at 135-137°.

The reaction mixture was treated with 100 ml of 0,2 N H_2SO_4, filtered, and extracted with methylene chloride. The resulting extract was washed with water and with a solution of $NaHCO_3$, and dried with $MgSO_4$. After distillation of the solvent and fractional distillation, there was obtained 4.3 g of pure ethyl α-phenetyl ether, m.p. 60.5-61.0° (8 mm). The substance did not possess optical activity ($[\alpha]_D^{21}$ = 0 ± 0.2°).

Found %: C 79.78; H 9.34. $C_{10}H_{14}O$. Calculated %: C 79.98; H 9.39.

5. Reaction of l-N-trimethyl-α-phenetylammonium iodide with n-butyl alcohol. 0.05 mole of l-N-trimethylammonium iodide (optical purity 59.8%) and 0.17 mole of dry butyl alcohol were heated under nitrogen in a flask with a reflux condenser for 5.5 hours at 12,5 ± 3°.

The reaction mixture was treated with 25 ml of H_2O and extracted with benzene.

The benzene solution of organic material was washed with water, with 2 N H_2SO_4, again with water, and with a 10% solution of soda, and was dried with K_2CO_3.

There was obtained 1.89 g of butyl α-phenetyl ether, b.p. 90.5-91.0° (8 mm), n_D^{20} 1.4812, d_4^{20} 0.902. The substance proved to be optically inactive ($[\alpha]_D^{23}$ = 0.1 ± 0.2°).

Found %: C 81.07; H 10.04. $C_{12}H_{18}O$. Calculated %: C 80.82; H 10.17.

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CONTRIBUTION TO THE QUESTION OF THE EFFECT OF INTERNAL HYDROGEN BONDING ON THE COLOR OF ORGANIC COMPOUNDS

I. S. Mustafin, L. O. Matveev and E. A. Kashkovskaya

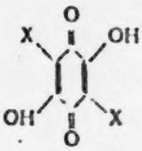
(Presented by Academician I. N. Nazarov, November 20, 1958)

Solutions of dihalo derivatives of 2,5-dihydroxy-p-benzoquinone or of haloanilic acids possess an interesting feature: with the addition of alkali, these violet-colored compounds change in color intensity without changing color. Such behavior is somewhat unusual, since similar colored, soluble organic compounds capable of splitting off a hydrogen ion acquire a deeper and more intense color if they change in the presence of alkali. It is not by chance that we have almost no single-colored indicators with a colorless alkaline form.

Contemporary chemical theory of color explains, in a specific manner, bathochromic and hyperchromic effects which usually accompany [illegible] in the pH of a solution of a colored organic substance having an acid character. Thus, for example, according to the theory of Dilthey and Wizinger, the transition of a colored substance into the ionoid state results in an increase in absorptive power, so that the color intensity of the ionoid compound frequently exceeds the color intensity of the corresponding nonionoid compound by more than a factor of 100 [1].

Actually, in those cases when the action of alkali leads, in the final analysis, to the filling of coordinative gaps, hypsochromic and hypochromic effects and even complete decoloration of the substance is observed. This is precisely what happens during the transition of colored carbonium salts into colorless carbonyl compounds, for example.

However, the haloanilic acids are structurally simple substances:



where X = Cl, Br or I.

The halogens in these compounds are stably bound, as follows both from the nature of their synthesis (the action of alkali on tetrahalo-p-benzoquinone) and from the fact that they react with silver ions, even under relatively severe conditions, with the formation of the corresponding haloanilates rather than silver halide.

During the identification of haloanilic acids prepared by us and purified according to existing methods [2-5], it was shown that they correspond to those described in the literature.* They are strong acids. The pH of their $5 \cdot 10^{-3}$ M solutions, calculated from electrical conductivity, were, respectively: for chloranilic acid, 2,41; for bromanilic acid, 2,32; for iodoanilic acid, 2,21. These data indicate that the hydrogen of the second hydroxyl of iodoanilic acid is appreciably ionized.

During solution of these substances and their reaction with alkalies, there is scarcely any disturbance of their molecular structure, so that the observed optical effect cannot be explained by this. Following the usual concepts, it is more easily assumed that solution, in this case, is accompanied by more or less further ionization, and the reaction with alkalies – by salt formation with subsequent complete decomposition into ions.

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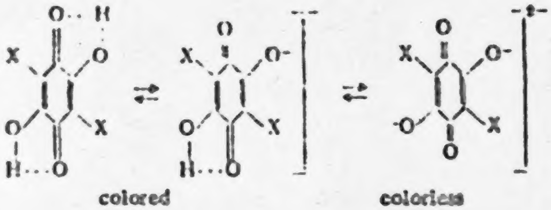
*F. G. Kazakova and R. I. Storozheva participated in the experimental work.

It should be noted that the study and explanation of the optical properties of the haloanilic acids has not only the well-known theoretical interest, but also a specific practical significance, since one of the compounds considered – chloranilic acid – is used as a colorimetric reagent for calcium [6-9].

As a result of a comparison of all the facts available to us, we were led to the conclusion that the dissociation of the haloanilic acids can be described by:



Thus, we consider that the idea of intramolecular hydrogen bonding provides a guiding thread for understanding the optical properties of the haloanilic acids.

The above structures of the acids and their step-wise dissociation can hardly provoke objections; the concept of the reversibility of the decomposition process and the emergence of internal hydrogen bonds can be substantiated not only by references to analogies, but also by energy considerations. As regards the effect of internal hydrogen bonds on the absorption spectra of organic compounds, this question has been considered in the literature in its various aspects [10-12].

The above scheme has a number of consequences. In the first place, upon dilution of solutions of haloanilic acids, the optical density of these solutions must decrease faster than would be expected from calculations based on the concentration of the dissolved substance.

In the second place, the addition to these solutions of strong mineral acids must be accompanied by an appreciable increase in color intensity, and the addition of alkalies – by a sharp decrease.

In the third place, the soluble salts of these acids must color solutions the same color as the acid.

In the fourth place, the molar extinction coefficients of the acids at maximum absorption must be considerably greater than those of the soluble salts.

In the fifth place, the addition to solutions of the acids of water soluble substances of low dielectric constant must lead to an increase in the color intensity of the solutions.

All of these consequences are in complete agreement with the experimental facts, which we now proceed to consider.

The haloanilic acids and their salts are respectively similar in optical properties, as the spectral curves, taken on a Pulfrich photometer (Figure 1), indicate.

The molar extinction coefficients of the acids ϵ_{mol_a} and salts ϵ_{mol_s} are also respectively similar for the spectral region around 550 mμ.

Acid	$\epsilon_{mol/a} \cdot 10^{-3}$	$\epsilon_{mol/s} \cdot 10^{-3}$
Chloranilic	0.77	0.18
Bromanilic	0.81	0.2
Iodoanilic	0.84	0.25

These data indicate that the molar coefficients of the haloanilic acids are 3-4 times greater than those of their salts.

On dilution of the solutions, the molar extinction coefficients of the haloanilic acids decrease, and, in connection with this, the degree of dissociation increases, as may be seen from the data on the change in ϵ_{mol} of chloranilic and iodanilic acids at λ_{max} in relation to concentration of the solution:

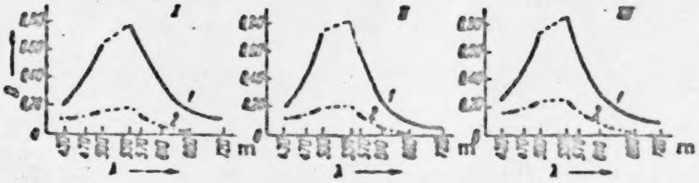


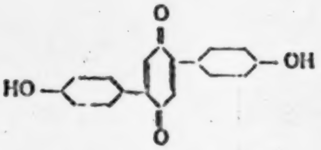
Fig. 1. Spectral curves of 0.002 M solutions of haloanilic acids (1) and their sodium salts (2): I) chloranilic, II) bromanilic, III) iodoanilic.

Concentration mol/liter	ϵ_{mol} chloranilic acid ($\times 10^{-3}$)	ϵ_{mol} iodoanilic acid ($\times 10^{-4}$)
0.[illegible]	0.77	0.84
0.0013	0.69	0.77
0.0006	0.66	0.74

In actuality, on dilution of solutions of haloanilic acids, their light absorption decreases to a greater extent than can be accounted for on the basis of the decrease in concentration. As regards ϵ_{mol}, it decreases by 15-20% on threefold dilution of the solution, i.e., by an amount outside experimental error.

An increase in color intensity is clearly observed on dilution with mineral acids of solutions of the substances studied to almost completely colorless solutions. A hyperchromic effect also accompanies the introduction into solutions of the acids of substances suppressing dissociation (acetone). The addition of alkalies to the brightly colored solutions, as pointed out above, sharply decreases color intensity.

For comparison with these compounds, we synthesized p,p'-dihydroxy-2,5-diphenylbenzoquinone [13]:



and satisfied ourselves that conversion of this substance into the ionoid state is accompanied by the usual bathochromic and hyperchromic effects: this substance, at $\lambda = 430$, has ϵ_{mol} of the order of $7.5 \cdot 10^3$, and the product of its reaction has ϵ_{mol} of $1.1 \cdot 10^4$ at $\lambda = 550$. This is to be expected, since, in this case, internal hydrogen bonds are not present in the molecule.

Thus, the facts considered in the present work must be taken into account during the use of haloanilic acids in colorimetry.

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ISOLATION OF β-BUTYLTHIOPHANE FROM PETROLEUM OF THE COAL-BEARING STRATA OF THE TUIMAZY FORMATION

R. D. Obolentsev and B. V. Aivazov

(Presented by Academician I. N. Nazarov, November 20, 1956)

Cyclic sulfides contained in petroleum fractions boiling above 200° have been studied very little. The investigations of Mabery [1] established the presence in kerosene distillate from Canadian petroleum of compounds boiling above 200° and having the general formula $C_nH_{2n}S$. To these compounds was given the name thiophanes. However, not one of them was isolated in the pure state and identified.

Up to the present, investigators of various countries have identified only one cyclic sulfide in petroleum products boiling above 200°, but it has been established that the cyclic sulfides contained in petroleum products belong to different homologous series [2-5].

In connection with the above, it seemed to us to be not without interest to report on β-butylthiophane which was isolated by us from petroleum of the coal-bearing strata of the Tuimazinsk formation. This petroleum was subjected to isothermal vacuum rectification, the kettle temperature being maintained at 135 ± 0,5° while the pressure was gradually decreased from atmospheric to 0,5 mm Hg. The entire apparatus was constructed from stainless steel and glass. The rectification produced 2 volume % of a fraction with a GOST boiling range of 12-18°. One of the fractions, boiling in the range 198-214° and containing 1,02% total sulfur, was chromatographed over MSM brand silica gel. For this purpose, the silica gel, which had a particle size of 0,5-0,25 mm, was poured into a brass chromatographic column having a height of 4,5 m and a diameter of 18 mm. The silica gel was completely wetted with the fraction being chromatographed, after which it was eluted with acetone. Three fractions were collected during the chromatographing process. Fraction I was a mixture of paraffinic and naphthenic hydrocarbons which contained no organosulfur compounds. Fraction II, the intermediate fraction, contained 1,31% total sulfur. Fraction III, after distillation of the acetone, was a mixture of aromatic hydrocarbons and organosulfur compounds. The total sulfur content of this fraction was 9,10%; hence, this fraction contained 68,6% of the sulfur contained in the fraction chromatographed.

Fraction III was subjected to a second chromatographing under the same conditions used for the 196-214° fraction. Two chromatographic fractions were isolated. The total sulfur content of I was 6,10% and that of II was 14,0%, where Fraction II contained 43,5% of the sulfur in the original 196-212° fraction. Fraction II was then dissolved in isooctane, and subjected to further chromatographing in a column 1 m high and 10 mm in diameter and filled with ShSM brand silica gel. The eluent in this case was a 1 : 1 (volume) mixture of benzene and acetone. Five fractions were collected; the eluent was distilled from each and the total sulfur content of each fraction was determined. Fraction V contained 22,4% total sulfur, which comprised 11,3% of the sulfur in the 196-214° fraction.

Fraction V from the third chromatographic fractionation was vacuum distilled. Density, refractive index, and elemental composition (semimicro method) were determined on the distillate. The content of sulfide sulfur, which was determined by potentiometric titration, was equal to the sulfur content obtained by elemental analysis. In addition, the Raman spectrum (ISP-51 spectrograph) and the absorption spectrum (in standard isooctane solution) in the ultraviolet region (ISP-22 spectrograph) were obtained.* Intensities were measured with an MF-2 microphotometer, and the wavelengths were measured with an IZA-2 comparator. The absorption spectrum in the ultraviolet region of the compound isolated is presented in Figure 1. In the literature available

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* The Raman spectrum was obtained by A. D. Biktasheva and the spectrum in the ultraviolet region by N. S. Lyubopytova.

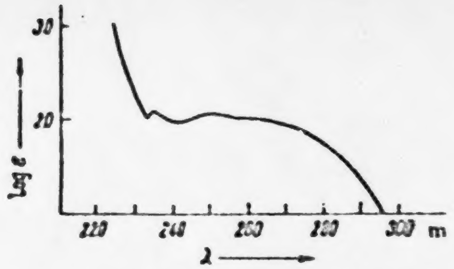

Fig. 1. Absorption spectrum of β-butylthiophane in the ultraviolet region.

to us, we did not encounter data on the ultraviolet absorption spectrum of β-butylthiophane.

The following properties indicate that the organosulfur compound isolated by us from petroleum of the coal-bearing strata of the Tuimazinsk formation and the β-butylthiophane synthesized by Yuryev [6] are identical.

d_4^{20} 0.9260 (lit. [6] 0.9271); n_D^{20} 1.4863 (lit. [6] 1.4868); Mol. wt.: Found 144, Calculated 144.27; b.p. 212°/760 mm (lit. [6] 209.5° – 209.9°/733 mm); R_D: Found 0.3105, Calculated 0.3101.

The lines in the Raman spectrum were characteristic of the thiophane ring ($\Delta\nu$) 687 ± 3 cm^{-1} (lit. [6] 690 cm^{-1}).

Found (wt. %): C 66.55; H 11.22; S 22.4. Calculated (wt. %): C 66.59; H 11.18; S 22.23.

Sulfide sulfur, determined potentiometrically (wt.%): found 22.4; calculated 22.23.

It should be noted that the β-butylthiophane was isolated by us from petroleum by means of only vacuum rectification and chromatography, while all of the sulfides reported in the literature as having been found in petroleum products were isolated through complex compounds of mercury salts.

The β-butylthiophane identified by us is the second cyclic sulfide boiling above 200° to be isolated from petroleum.

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ON THE REACTION OF IOTSITCH REAGENT WITH Δ²-CYCLOPENTENYL CHLORIDE

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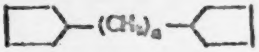
(Presented by Academician B. A. Kazansky, November 2, 1958)

Inasmuch as the cyclopentane hydrocarbons of the general formula



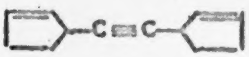
have been insufficiently studied, we undertook the synthesis of several of these hydrocarbons. In particular, the use of the reaction between Δ²-cyclopentenyl chloride and Iotsitch reagent was contemplated for the preparation of 1,2-dicyclopentylethane, one of the members of this series. As is well known, Iotsitch reagent consists primarily of acetylenedimagnesium bromide (according to the data of Grignard and co-workers [1], up to 95%) and a certain amount of acetylenemonomagnesium bromide. It is known from published data that Iotsitch reagent reacts with alkyl halides only with difficulty. For example, 3-hexyne is formed in only 20% yield by the action of ethyl bromide on acetylenedimagnesium bromide [2]. Usually, the action of Iotsitch reagent on alkyl halides is accompanied by side reactions, of which the principal ones are the splitting out of hydrogen halide from the alkyl halide and the reduction of the alkyl halide to the corresponding alkane. Thus, considerable amounts of butylene and butane are liberated by the reaction of acetylenedimagnesium bromide with n-butyl bromide, while the reaction with n-octyl bromide yields n-octane as the chief reaction product [3]. There is no information in the literature on the reaction of Iotsitch reagent with halogen derivatives of cyclic hydrocarbons.

TABLE 1

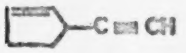
Reaction of Δ²-Cyclopentenyl Chloride with Iotsitch Reagent

Experiment No.	Amount of reagent used (moles)			Yield (I)		Yield (II)	
	for preparation of Iotsitch reagent		cyclopentenyl chloride	g	% theoretical	g	% theoretical
	ethyl bromide	[illegible]					
1	1	1	0.8	19	31		not isolated
2	2	2	1.25	35	28	20	25
3	2	2	2	32	20	23	20
4	2	2	1.6*	37	30.5	21	23

In Δ²-cyclopentenyl chloride, which is easily prepared from cyclopentadiene, the chlorine atom is allylic and, therefore, very reactive. For this reason, Δ²-cyclopentenyl chloride has been repeatedly used in reactions with alkylmagnesium halides for the preparation of Δ²-alkylcyclopentenes [4]. In the present work, we studied the reaction of Δ²-cyclopentenyl chloride with Iotsitch reagent, and showed that di-Δ²-cyclopentenylacetylene (I) is formed in an amount of 20-30%; however, approximately the same amount (20-30%) of Δ²-cyclopentenylacetylene (II) is formed simultaneously.



(I)



(II)

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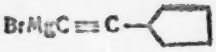
* 4 g cuprous chloride added to the reaction mixture.

Attempts to increase the yield of di-Δ^2-cyclopentenylacetylene by changing reaction conditions (different reagent ratios, the introduction of cuprous chloride as a catalyst) failed. The data obtained are presented in Table 1.

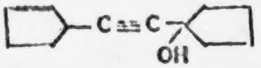
The constant amount of both possible reaction products, independent of the amount of reagents used, and the considerable yield of Δ^2-cyclopentenylacetylene can apparently be explained by different rates of reaction of Δ^2-cyclopentenyl chloride with both of the possible organomagnesium compounds:

$BrMgC \equiv CMgBr$;



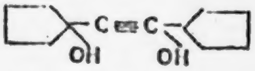
As the Δ^2-cyclopentenyl chloride was added to the Iotsitch reagent, magnesium salts were included in the precipitate, the reaction mixture thickened, and the reaction ceased, although both organomagnesium compounds and chloride were still present in the mixture. The excess chloride was gradually converted into a polymeric tar with the liberation of hydrogen chloride.

In one experiment, after the addition of approximately half of the required amount of Δ^2-cyclopentenyl chloride to the Iotsitch reagent, cyclopentanone was added, which, as is well known[5], can react with this reagent to give up to 77% of the corresponding glycol. After decomposition of the reaction mixture, all possible reaction products were found in it, namely: Δ^2-cyclopentenylacetylene, di-Δ^2-cyclopentenylacetylene, and also the tertiary alcohol



(III)

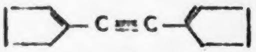
and the glycol 1,2-di-(1-hydroxycyclopentyl)acetylene.



(IV)

The presence of the latter two compounds shows that both the mono- and the di-magnesium organic compounds were present in the reaction mixture at the time the cyclopentanone was added.

The di-Δ^2-cyclopentenylacetylene (I) is an isomer of a previously synthesized hydrocarbon with a conjugated system of multiple bonds, di-Δ^1-cyclopentenylacetylene



which has an m.p. of 58.5-60° and a b.p. of 105-110° at 2 mm [5].

By hydrogenation of di-Δ^2-cyclopentenylacetylene in the cold, under hydrogen pressure, and in the presence of Raney nickel, the saturated hydrocarbon 1,2-dicyclopentylethane was obtained.

EXPERIMENTAL

The Iotsitch reagent was prepared by the method described by Pinkney and Marvel [5]. The cyclopentenyl chloride was prepared by the addition of hydrogen chloride to cyclopentadiene [6].

The reaction of Iotsitch reagent with cyclopentenyl chloride. The experimental results are presented in Table 1. Below is given a description of Experiment 4. The magnesium derivative was prepared from 2 moles of ethyl bromide and 2 g-atoms of magnesium in 1.2 liters of absolute ether in a two-liter flask fitted with a stirrer, a dropping funnel, and a reflux condenser. Acetylene (about 30 liters) was passed through the solution of organomagnesium complex until there was a well-defined separation of Iotsitch reagent and ether. While cooling the reaction flask to − 10 to − 15° with an ice-salt mixture, 164 g (1.6 mole) of Δ^2-cyclopentenyl chloride in 200 ml of absolute ether was added drop-wise, and then 4 g of cuprous chloride, after which the mixture was stirred for an additional 3 hours at room temperature and 6 hours while heating on a water bath. 200 ml of water and then 300 ml of dilute sulfuric acid were added, while cooling with ice and salt, to decompose the complex. The ether layer was washed with water, soda, again with water, and dried with calcium chloride. After distillation of the ether, the light ends were distilled under a slight vacuum to 90° at 90-100 mm. Distillation of this fraction in a column of 40 theoretical plates gave 21 g (28 % of theoretical) of Δ^2-cyclopentenylacetylene (II) having the following properties: b.p. 97.2° at 752 mm; n_D^{20} = 1.4363 d_4^{20} = 0.8014; found MR_D = 30.10; calculated for $C_7H_8 \vDash_3 \vDash$ MR_D 29.60.

In order to prove the structure of the Δ^2-cyclopentenylacetylene, 15 ml of the hydrocarbon was hydrogenated in alcoholic solution (25 ml) in the cold, under hydrogen pressure, and in the presence of 5 g of Raney nickel. Ethylcyclopentane having the following constants was obtained: b.p. 102.8° at 750 mm; n_D^{20} = 1.4198; d_4^{20} = 0.7663. Literature data [7]: b.p. 103.466° at 760 mm; n_D^{20} = 1.41931; d_4^{20} = 0.76647.

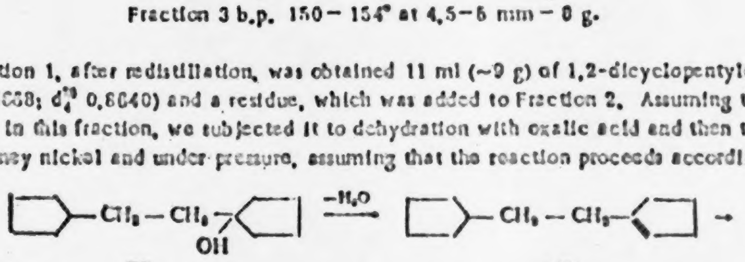
After distillation of the Δ^2-cyclopentenylacetylene from the reaction mixture, 37 g of the fraction boiling at 96-102° at 8 mm was dis under a higher vacuum, and was redistilled under vacuum in a column with 15 theoretical plates. 32 g of di-Δ^2-cyclopentenylacetylene having the following properties was obtained: b.p. 106°/9-9.5 mm; n_D^{20} = 1.5172; d_4^{20} = 0.9598; found MR_D = 49.83; for $C_{12}H_{14} 2\vDash, \vDash_3$ calculated MR_D 50.20.

For proof of structure, 15 ml of di-Δ^2-cyclopentenylacetylene was hydrogenated in the cold, in an autoclave at 70-80 atm., in solution in 75 ml of ethyl alcohol, and in the presence of 15 g of Raney nickel. The catalyzate was washed with water to remove the alcohol, and to eliminate traces of unsaturated hydrocarbons, it was chromatographed over 15 g of silica gel. There was obtained 14 ml of a preparation, which was vacuum-distilled in a column with 40 theoretical plates. After the distillation, 12 ml of the hydrocarbon was again chromatographed with 10 g silica gel. 10 ml of 1,2-dicyclopentylethane with the following properties was obtained: b.p. 92° at 8-8.5 mm; n_D^{20} = 1.46628; d_4^{20} = 0.8620; found MR_D 53.33; for $C_{12}H_{22}$ calculated MR_D 53.23. The following data for this hydrocarbon, prepared by a different method, are given in the literature (5): b.p. 109-110° at 17 mm; n_D^{20} 1.4657; d_4^{20} = 0.8633.

Reaction of Iotsitch reagent with Δ^2-cyclopentenyl chloride and cyclopentanone in two stages. 78 g (0.75 mole) of Δ^2-cyclopentenyl chloride in 150 ml of absolute ether was added drop-wise, while cooling with ice and salt, to Iotsitch reagent prepared as described above from 2 moles of ethyl bromide and 2 g-atoms of magnesium in 1.2 liters of absolute ether. The mixture was stirred at room temperature for 4 hours, after which 63 g (0.75 mole) of cyclopentanone in 150 ml of absolute ether was added while cooling. The reaction mixture was stirred for 3 hours at room temperature and 4 hours while heating on a water bath. Decomposition and further treatment was carried out as in the preceding experiment. There were obtained 7 ml (~ 6 g) of Δ^2-cyclopentenylacetylene (II) (b.p. 97-98°; n_D^{20} = 1.4365) and a broad fraction boiling at 122-170° at 14 mm (57 g), which crystallized out in the receiver. This fraction was dissolved in 100 ml of alcohol, and hydrogenated in the cold, under a pressure of 70-80 atm., in the presence of 13 g of skeletal nickel. After distillation of the alcohol, the residue was distilled under vacuum:

Fraction 1 b.p. 92 − 125° at 5 mm − 22 g
Fraction 2 b.p. 125 − 150° at 5 mm − 23 g
Fraction 3 b.p. 150 − 154° at 4.5−5 mm − 8 g.

From Fraction 1, after redistillation, was obtained 11 ml (~9 g) of 1,2-dicyclopentylethane (b.p. 87° at 6 mm; n_D^{20} = 1.4658; d_4^{20} 0.8640) and a residue, which was added to Fraction 2. Assuming that the tertiary alcohol (V) could be in this fraction, we subjected it to dehydration with oxalic acid and then to hydrogenation in the cold with Raney nickel and under pressure, assuming that the reaction proceeds according to:



In fact, after purification of the catalyzate by chromatographing with silica gel and distillation, there was obtained 8 g of 1,2-dicyclopentylethane (b.p. 92° at 8 mm; n_D^{20} = 1.4664; d_4^{20} = 0.8625).

Fraction 3 was twice recrystallized from acetone. 6 g of the glycol 1,2-di(1-hydroxycyclopentyl)ethane, m.p. 131-132°, was obtained. Literature data for this glycol [8]: m.p. 131.2-132.4°.

Found %: C 72.67; H 11.19. $C_{12}H_{22}O_2$. Calculated %: C 72.71; H 11.12.

Apparently, this glycol was formed by hydrogenation of glycol IV.

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* Russian translation.

ALLENE-ACETYLENIC ISOMERIC TRANSFORMATIONS IN SILICOHYDROCARBON SERIES

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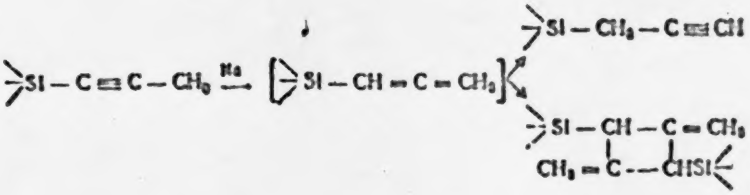
The isomeric transformations of disubstituted acetylenic hydrocarbons into monosubstituted and vice versa, discovered by A. E. Favorsky [1], and also the mechanism of these conversions, which proceeds through an allenic hydrocarbon stage, has already been the subject of many investigations [2]. The synthesis of silicoacetylenic hydrocarbons has also been described in a number of papers [3-8], but as regards isomeric transformations of acetylenic silicohydrocarbons, there has been only one investigation devoted to this reaction. It was shown [7] that disubstituted silicoacetylenic hydrocarbons with a triple bond in the α-position to the silicon (trialkyl-β-methylacetylenylsilanes) are isomerized on heating with sodium to monosubstituted silicoacetylenic hydrocarbons, but in small yield since the α,β-silicoallenic hydrocarbons formed as an intermediate product undergo cyclodimerization to compounds of type (2).


(1)

(2)

In the present investigation, β,γ-silicoallenic hydrocarbons were prepared for the first time by the condensation of Grignard reagents prepared from α-silicohalides with propargyl bromide. It is interesting to note that this gave only silicoallenic hydrocarbons, in 60-70% yield, probably according to:

$$\gt Si-CH_2MgCl+BrCH_2-C\equiv CH\rightarrow[BrCH=C=CH_2]\rightarrow\gt Si-CH_2-CH=C=CH_2.$$

A mixture of acetylenic and allenic hydrocarbons is formed by the condensation of Grignard reagents prepared from nonsilicon-containing halides with propargyl bromide [9]. On heating with sodium, the β,γ-silicoallenic hydrocarbons were converted in high yield (of the order of 40%) to monosubstituted silicoacetylenic hydrocarbons with the triple bond in the γ-position to the silicon. These silicohydrocarbons gave a white precipitate with a solution of silver nitrate. The monosubstituted acetylenic hydrocarbons with the triple bond γ to the silicon, in contrast to silicoacetylenic hydrocarbons with the triple bond in the α or β positions [3,6], undergo hydration with the formation of the corresponding ketones. In particular, we hydrated $(CH_3)_3Si-CH_2-CH_2-C\equiv CH$ and also $(CH_3)(C_2H_5)Si-CH_2-CH_2-C\equiv CH$ in the presence of the methanol solution of $HgSO_4$.

The sodium derivatives of the acetylenic silicohydrocarbons readily condensed with alkyl halides:

EXPERIMENTAL

Trimethylsilylmethylallene (siliconeopentylallene) $(CH_3)_3Si-CH_2-CH=C=CH_2$ (I). 119 g of propargyl bromide was added over a period of 3 hours, while stirring, to a Grignard reagent prepared from 26.4 g Mg and 134.6 g of $(CH_3)_3SiCH_2Cl$ in 350 ml of ether. Owing to the vigorous evolution of heat which occurred during the addition of the propargyl bromide, it was necessary to provide considerable cooling for the flask. At the conclusion of the addition of the bromide, the contents of the flask were heated on a water bath for 3 hours. After separation of the residue, the ether layer was dried with $CaCl_2$. After distillation of the ether, the reaction product, 130 g, was fractionated in a column with glass packing. There was obtained 90 g of a fraction boiling at 119.5-119.7°, which, according to the analytical data (Table 1) and the data from the spectroscopic investigation, proved to be $(CH_3)_3Si-CH_2-CH=C=CH_2$. The following frequencies (in cm^{-1}) appeared in the Raman spectrum: 148(4b), 173(4), 212(4), 240(4), 513(5), 612(8), 698(5b), 769(2), 836(3), 872(2), 940(3b), 1124(8), 1160(4), 1195(3), 1220(4), 1250(2), 1282(2), 1330(4), 1383(2), 1413(3), 1444(3), 2116(1), 2900(10), 2925(3), 2960(7), 2988(9), 3048(2). In the spectrum of I, as well as of II and III,* there was an intense line at 1124 cm^{-1}, corresponding to a symmetrical vibration of the cumulated double bonds [10,11]. The absence of observable lines in the 1600-1640 cm^{-1} region negates the possibility of the formation of dienic compounds. Along with this, a weak line was found at 2116 [1], which relates to the $C\equiv C$ frequency (IV). The amount of (IV) was quite small, ~5%.

Dimethylethylsilylmethylallene (II) and 4-(methyldiethylsilyl)methylallene (III) were synthesized under similar conditions; their properties are also presented in Table 1.

Trimethylsilylethylacetylene $(CH_3)_3Si-CH_2-CH_2-C\equiv CH$ (IV). 28 g of $(CH_3)_3Si-CH_2-CH=C=CH_2$, 5 g of finely shaved metallic sodium, and 50 ml of o-xylene with a b.p. of 144°** were placed in a flask fitted with reflux condenser. The contents of the flask were refluxed for 10 hours. Hydrogen was liberated, and the color of the mixture turned brown. The unreacted allenic silicohydrocarbon and part of the o-xylene were distilled. The residue was treated first with methyl alcohol and then with water in order to separate out the acetylenic silicohydrocarbon and to destroy the excess sodium. The organic reaction products were extracted with ether. Fractionation in a column gave 10 g of a fraction boiling at 115.5-116°, the analytical data and properties of which are presented in Table 1. The following lines appeared in the spectrum of IV (in cm^{-1}): 173(1), 212(2b), 241(3b), 278(0), 312(1), 336(3), 360(4), 460(4), 575(7), 608(7), 695(5), 835(1b), 898(2b), 945(2b), 1010(4), 1126(4b), 1155(3b), 1180(3b), 1252(3), 1280(1), 1321(3), 1411(4), 1437(2), 2116(10), 2845(3b), 2895(10), 2910(3), 2954(8), 3305(2). The characteristic frequencies are 2116 ($C\equiv C$) and 3305 cm^{-1} ($\equiv C-H$) [12]. 4-Dimethylethylsilyl-1-butyne $(CH_3)_2(C_2H_5)Si-CH_2-CH_2-C\equiv CH$ (V) and methyldiethylsylyl-1-butyne $(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv CH$ (VI) were prepared under similar conditons; their properties are presented in Table 1. All three representatives of the silicoacetylenic hydrocarbon series were distilled without polymerization. Of the isomeric allenicsilicohydrocarbons, only the first member of the series distilled without polymerization.

Siliconeopentylacetone $(CH_3)_3Si-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ (VII). 50 ml of methyl alcohol, 10 g of $(CH_3)_3SiCH_2-CH_2-C\equiv CH$ and 0.1 g $HgSO_4$ were introduced into a flask fitted with a stirrer and a reflux condenser. The contents of the flask were heated to the boiling point of methyl alcohol for 3 hours while stirring. After each hour, 0.01 g $HgSO_4$ was added to the mixture. The liquid was decanted from the gray catalyst residue, the methyl alcohol was distilled, and the reaction product was fractionated. 7 g of a fraction boiling at 82-83° at 64 mm was isolated; n_D^{20} 1.4223, d_4^{20} 0.8331; MR_D found 44.0; MR_D calculated 44.10. The ketone formed a dinitrophenylhydrazone melting at 102°. These properties agree closely with the properties of this ketone prepared by us by another reaction [13].

1-Methyldiethylsilyl-3-butanone $(CH_3)(C_2H_5)_2Si-CH_2-CH_2-\overset{/}{C}-CH_3$ (VIII) was prepared by the hydration of $(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv CH$ under the conditions of the synthesis of (VII); b.p. 85° at 10 mm, n_D^{20} 1.4410, d_4^{20} 0.8624.

Found %: C 62.09; H 11.98; Si 15.70. $C_9H_{20}SiO$. Calculated %: C 62.34; H 12.21; Si 16.20.

The 2,4-dinitrophenylhydrazone of this ketone melted at 78-79°.

Found %: N 16.21. $C_{15}H_{24}SiN_4O_4$. Calculated %: N 15.90.

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* The spectra of (II), (III), (V), and (VI) will be published later.

** In subsequent experiments, the o-xylene was replaced by a kerosene fraction boiling in the range 220-230°.

TABLE 1

No.	Compound	B. p., °C	Press, mm Hg	n_D^{20}	d_4^{20}	MR		Yield, %	C, %		H, %		Si, %	
						found	calc.		found	calc.	found	calc.	found	calc.
I	$(CH_3)_3Si-CH_2-CH=C=CH_2$	119.5–119.7	755	1.4452	0.7865	42.73	42.56	72	66.12; 66.17	66.59	11.52; 11.72	11.18	21.81; 22.28	22.22
II	$(CH_3)_2(C_3H_7)Si-CH_2-CH=C=CH_2$	63	15	1.4632	0.8041	52.87	52.49	79	70.20; 69.90	70.05	11.80; 11.80	11.69	—	—
III	$(CH_3)_2(C_2H_5)Si-CH_2-CH=C=CH_2$	145	752	1.4478	0.7911	47.48	47.87	83	67.62; 67.55	68.51	11.58; 11.53	11.48	19.29; 20.01	20.00
IV	$(CH_3)_3Si-CH_2-CH_2-C\equiv CH$	115.5–116	754	1.4235	0.7620	42.1	42.56	50	66.03; 66.19	66.59	11.22; 11.30	11.18	21.85; 21.67	22.22
V	$(CH_3)_2(C_2H_5)Si-CH_2-CH_2-C\equiv CH$	142	745	1.4310	0.7863	48.41	47.19	50	67.52; 67.42	68.51	11.60; 11.40	11.48	19.78; 19.34	20.00
VI	$(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv CH$	59–60	15	1.4435	0.8020	51.08	51.81	50	69.71; 69.80	70.05	11.85; 12.01	11.69	17.88	18.18

1-Methyldiethylsilyl-3-octyne $(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_3$ (IX). To the sodium derivative of $(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv CH$, prepared by the above-described method from 15.4 g of $(CH_3)(C_2H_5)_2Si-CH_2-CH=C=CH_2$, was added 27.4 g of C_4H_9Br. The mixture was refluxed for 3 hours. The organic products were extracted with ether. Fractionation gave 6 g of a fraction with a b.p. of 90-91.5° at 8 mm; n_D^{20} = 1.4570; d_4^{20} = 0.8227; MR_D found 69.77; MR_D calculated 70.34.

Found %: C 73.67; H 12.46; Si 13.30. $C_{13}H_{26}Si$. Calculated %: C 74.19; H 12.45; Si 13.35.

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* As in original; this probably should read Doklady Akad. Nauk SSSR 72, 1839 (1950) – Publisher's note.

** Original Russian pagination. See C. B. translation.

ON THE VAPOR-PHASE OXIDATION OF STYRENE AND α-METHYLSTYRENE OVER TIN VANADATE

B. V. Suvorov, S. R. Rafikov, A. V. Solomin and M. I. Khmura

(Presented by Academician B. A. Arbuzov, October 3, 1958)

The investigation of oxidative conversions of unsaturated compounds by molecular oxygen in the presence of heterogeneous catalysts is important for the clarification of the mechanism of the catalytic oxidation of organic compounds, which is presently widespread in commercial organic synthesis. Of definite interest in this regard is the study of the vapor-phase catalytic oxidation of organic compounds with a double bond in a side chain, since they are probable intermediate products in the oxidation of alkylbenzenes [1]. Literature data on this problem is extremely scanty; in particular, we found no information on the vapor-phase oxidation of the objects of this investigation – styrene and α-methylstyrene – with atmospheric oxygen over vanadium catalysts.

Our starting materials had the following properties: styrene – b.p. 52°/28 mm, n_D^{20} = 1,5460, d_4^{20} = 0,909; α-methylstyrene – b.p. 62°/20 mm, $n_D^{17.5}$ = 1,5331, d_4^{20} = 0,897. The experiments were carried out in a flow-type apparatus with a contact time of 0,08-0,10 seconds and a space rate of 0,10-0,12. Moisture-containing air with a water content of up to 300 g/cu.m. was used as the oxidant. The catalyst was granular tin vanadate.

The major oxidation products of both of the hydrocarbons studied were benzoic acid and maleic anhydride. Their determination was carried out by the usual method, titration with alkali [2]. In separate experiments, they were isolated in the pure form as a check. In the reaction products of all experiments, in addition to the acids, quinone, formaldehyde, carbon monoxide, and carbon dioxide were present. Moreover, benzaldehyde was observed in the oxidation of styrene, and acetophenone in the oxidation of α-methylstyrene. The quinone was quantitatively determined iodometrically [3], and was identified by the formation of hydroquinone with a m.p. of 171°. Quantitative determination of formaldehyde was based on the formation of the dimedon derivative (m.p. 187°). Benzaldehyde and acetophenone were isolated from the oily reaction products by distillation after first washing with water and drying. The benzaldehyde had a b.p. of 176°/700 mm, n_D^{20} = 1,5450; its semicarbazone melted at 220-221°. The acetophenone boiled at 95°/33 mm, n_D^{20} = 1,5367; its semicarbazone melted at 196°. Determination of CO and CO_2 was carried out by the usual methods of gas analysis with a VTI apparatus.

The results of the experiments on the oxidation of styrene and α-methylstyrene are presented in Tables 1 and 2. As seen from the data presented, the yield of specific oxidation products from each of the initial materials depends on reaction temperature; an increase in reaction temperature contributes to the progressive destruction of the hydrocarbon skeleton of the compound oxidized. Thus, in experiments carried out at a relatively low temperature, benzoic acid and compounds with an unchanged aromatic ring predominated among the reaction products. At an elevated temperature, their yield decreased, and the amount of quinone and maleic anhydride increased.

A very characteristic index was the amount of low molecular weight products formed by complete and incomplete oxidation. As seen from the data presented, the total amount of formaldehyde, CO and CO_2 at low temperatures did not exceed 1,25 mole per mole of oxidizable hydrocarbon. This indicates that the low molecular weight products were formed chiefly at the expense of oxidation of the side chains. At high temperatures, the amount of low molecular weight products reached 2,4 mole/mole (in the case of α-methylstyrene). Under these conditions, part of the low molecular weight products were formed at the expense of destruction of the benzene ring with the formation of maleic anhydride and products of its decomposition. It should be

TABLE 1

Yield of Major Oxidation Products of Styrene

Experiment No.	Temperature, °C	Yield of products of incomplete oxidation in % of theoretical based on starting material charged			
		benzaldehyde	benzoic acid	quinone	maleic anhydride
1	285	7.8	30.3	—	5.3
2	309	3.3	53.4	0.5	6.4
3	320	Trace	54.5	0.7	9.6
4*	330	•	57.8	0.3	11.4
5	340	•	57.1	0.8	10.5
6	350	•	48.8	0.8	10.9
7	360	•	43.0	0.7	13.3
8**	374	•	35.0	0.7	12.7
9	385	•	31.8	0.2	17.3
10	400	•	23.1	0.1	15.6

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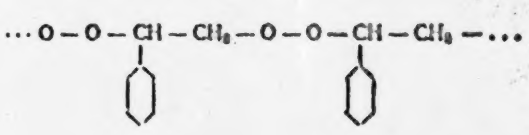
* In Experiment No. 4, the following were also determined: formaldehyde (0.11 mole/mole of styrene), carbon monoxide (0.96 mole/mole), carbon dioxide (0.12 mole/mole).

** In Experiment No. 8: formaldehyde (0.09 mole/mole), carbon monoxide (1.06 mole/mole), and carbon dioxide (0.42 mole/mole).

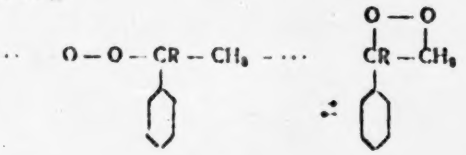
noted that carbon monoxide was the major low molecular weight product, which indicates its high stability under the experimental conditions used.

These results provide a basis for the assumption that, in the initial stages, the oxidation of styrene and α-methylstyrene proceeds in the same direction as in the condensed phase in the presence or absence of catalysts [4,5]. There are indications [6] that, under mild conditions and in the absence of catalysts, the reaction of styrene with molecular oxygen proceeds with the formation of polymeric peroxides of the type



$$\cdots O-O-CH-CH_2-O-O-CH-CH_2-\cdots$$

It is quite probable that the initial stage of the formation of such peroxides is the addition of oxygen to a molecule of styrene or α-methylstyrene with the formation of unstable peroxides of the following structure:



where, R = H, CH$_3$.

Under the conditions of vapor phase oxidation, the formation of polymeric peroxides is impossible in view of the high temperature and the low concentration of reacting components. Thermal decomposition with the formation of benzaldehyde and formaldehyde in the case of styrene and of acetophenone in the case of α-methylstyrene is more probable. The experimental data presented in Tables 1 and 2 corroborate such an assumption. At relatively low reaction temperatures, it was possible to isolate from the catalyzate appreciable amounts of the expected products of the conversion of monomeric peroxides.

TABLE 2

Yield of Major Oxidation Products of α-Methylstyrene

Experiment No.	Reaction temperature, °C	Yield of oxidation products						
		In % of theoretical				In moles per mole of starting material		
		acetophenone	benzoic acid	quinone	maleic anhydride	CH$_2$O	CO	CO$_2$
11	310	0.4	25.2	0.2	10.1	Not det.	Not det.	Not det.
12	330	2.3	54.3	0.7	17.5	0.22	0.88	0.15
13	342	Trace	61.2	1.1	16.6	0.24	1.31	0.11
14	354	•	56.0	1.4	18.0	0.24	1.54	0.14
15	366	•	47.5	1.4	20.6	0.23	1.69	0.18
16	378	•	44.5	1.8	22.8	0.25	1.83	0.16
17	390	•	40.0	1.8	23.8	0.20	1.95	0.20

At higher temperatures, acetophenone and benzaldehyde were not found in the reaction products, since they underwent further oxidation with successive conversion to benzoic acid, benzoquinone, and maleic anhydride [1,2].

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INVESTIGATION IN THE FIELD OF PIAZOTHIOLE (3,4-BENZO-1,2,5-THIADIAZOLE) CHEMISTRY

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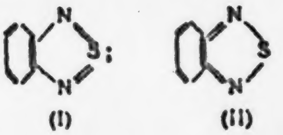
(Presented by Academician I. N. Nazarov, November 20, 1958)

In previous communications [1] we presented data characterizing the aromatic properties of benzo-2,1,3-thiadiazole. Of the several possible structures, the following structures (I) and (II) correlate best with this compound:



(I) (II)

The synthesis of benzo-2,1,3-thiadiazole from o-phenylenediamine and thionyl chloride (or sulfur dioxide) [2] indicates structure (I); the clearly expressed aromatic character and the high stability of piazothiole toward various chemical agents (oxidizing agents, acids, alkalies) can be explained by either structure [2,3]. Data from physical investigations [4] also do not provide a definite indication relative to the structure of this heteroselenodiazole and its 5-chloro derivative, which were investigated by Hill and Sutton [5], permit assignment of structure (II) to the first two substances and of either structure (I) or (II) to the second two substances. Measurements of the interatomic distances, carried out by Luzzati [4], also permits assignment of either structure.

It would seem that if benzo-2,1,3-thiadiazole has the structure (II), it would possess a certain unsaturation. Clarification of the unsaturated nature of this heterocycle is the more important, since the available experimental data indicated only its aromatic nature. As regards chemical properties which could indicate the presence of a quinoid structure, such data have not been confirmed by anyone; on the contrary, according to recently published data [3], piazothiole cannot undergo addition reactions.

However, investigations carried out by us showed that piazothiole vigorously (with the liberation of heat) adds both chlorine and bromine; the reaction was carried out both in the melt and in organic solvents (chloroform, dichloroethane, etc.) and in the presence or absence of catalysts (iron filings). The reaction products were the corresponding tetrachloro- or tetrabromotetrahydrobenzo-2,1,3-thiadiazole, which were formed as a mixture of stereoisomers.

By fractional crystallization of the tetrachlorotetrahydrobenzo-2,1,3-thiadiazoles we obtained from the mixture two isomers with melting points of 123-124° and 82°. By treatment of the tetrachlorotetrahydro derivatives with an alcoholic solution of sodium hydroxide, we obtained the dihalopiazothioles, the structure of which was proved by a second synthesis from the corresponding dihalo-o-diamines and thionylaniline [N-sulfinylaniline].

Thus, the data obtained permit the assumption that by the reaction of piazothiole with chlorine (or bromine), the addition of four atoms of halogen takes place with the formation of the tetrahalotetrahydro derivatives, which by reaction with an alcoholic solution of an alkali split out two molecules of hydrogen halide (HCl or HBr) with the formation of the dihalo derivatives according to:

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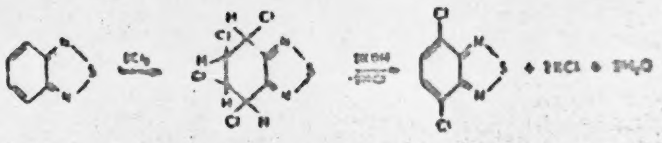
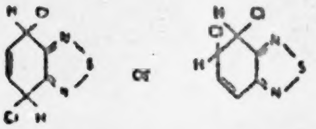
* Russian translation.



L. S. Efros and R. M. Levit, studying, recently, the reaction of piazothiole with chlorine, found that dichloropiazothiole of the above structure is formed most rapidly.

Of the four isomers synthesized by us – representing all of the structures for dichloropiazothioles predictable by theory – not one corresponded to the substance melting at 87.5° described by these authors. Therefore, it was possible that the latter compound was the product of the partial addition of chlorine to piazothiole of the structure:



With the aim of verifying this assumption, we carried out the chlorination of piazothiole with stoichiometric amounts of chlorine (corresponding by weight to two atoms of chlorine). After distillation under vacuum, in addition to unreacted benzo-2,1,3-thiadiazole, only tetrachlorotetrahydrobenzo-2,1,3-thiadiazole was detected; treatment of the latter with an alcoholic solution of potassium hydroxide gave 4,7-dichlorobenzo-2,1,3-thiadiazole.

In further investigations in the field of the halogenation of derivatives of piazothiole, we established that 5-methyl, 5-bromo-, and other piazothiole derivatives also react with chlorine (or bromine); it was also shown that 1',2'-naphtho-2,1,3-thiadiazole adds chlorine (or bromine). Thus, the experimental data show that piazothiole (and also 1',2'-naphtho-2,1,3-thiadiazole) and its derivatives possess properties characteristic of unsaturated compounds in addition to those of aromatics.

EXPERIMENTAL

Chlorination of benzo-2,1,3-thiadiazole. Chlorine was passed into a melt of 13.6 g of benzo-2,1,3-thiadiazole at 60° until the weight had increased 7.1 g (corresponding to two atoms of chlorine). Four fractions were obtained by distillation. Fraction I: b.p. to 140° (20-30 mm), 6 g, m.p. 42-44°, no melting point depression when mixed with piazothiole; Fraction II: b.p. 141-150° (20-30 mm), 2 g, clear, oily liquid which did not crystallize during storage. Treatment of the latter with an alcoholic solution of potassium hydroxide gave a substance with m.p. of 175-178° and which melted without lowering of the melting point when mixed with 4,7-dichlorobenzo-2,1,3-thiadiazole. Fraction III: b.p. 151-185° (20-30 mm), 3.5 g, oily liquid, crystallized during storage; after recrystallization from alcohol, m. p. 75-82°. A mixture with tetrachlorotetrahydrobenzo-2,1,3-thiadiazole (m.p. 82°) melted without depression of the melting point. Fraction IV: b.p. 186-195° (20-30 mm); 4 g, oily liquid which crystallized rapidly. After recrystallization from alcohol, m.p. 175-178°; a mixture with 4,7-dichlorobenzo-2,1,3-thiadiazole melted without depression of the melting point.

Investigation of the chlorination of benzo-2,1,3-thiadiazole was carried out by another route; 35 g of the substance was mixed with 80 ml of alcohol while heating, the alcoholic solution, which separated from the oily liquid, gave, on cooling with ice-salt mixture, a substance, repeated recrystallization of which gave 3.5 g of a material (22% of theoretical) with m.p. of 120-124°. This substance was in the form of white needles which were soluble in alcohol, chloroform, dichloroethane, and benzene, sparingly soluble in petroleum ether, and insoluble in water.

Found %: C 25,95, 26,10; H 1,45, 1,62; N 10,34, 10,05; S 11,30, 11,63; Cl 51,44, 51,03.
$C_6H_4N_2SCl_4$. Calculated %: C 25,80; H 1,44; N 10,07; S 11,51; Cl 51,03.

The oily liquid, after heating with 50 ml of alcohol and subsequent cooling, gave by repeated fractional crystallization 1,4 g of a crystalline material with m.p. of 82°, which was soluble in alcohol, chloroform, and benzene, sparingly soluble in petroleum ether, and insoluble in water.

Found %: C 26,68, 25,90; H 1,66, 1,47; N 10,22, 10,09; S 11,87, 11,78; Cl 52,02, 51,90. $C_6H_4N_2SCl_4$.
Calculated %: C 25,80; H 1,44; N 10,07; S 11,51; Cl 51,03.

4,7-Dichlorobenzo-2,1,3-thiadiazole. a) 3,8 g of thionylaniline, b.p. 198-200°, was added with constant stirring to a suspension of 3,6-dichloro-1,2-phenylenediamine, m.p. 95-97°, in 5 ml of benzene. After heating on a water bath for 30 minutes, the reaction mixture was cooled, the precipitate filtered and, after washing with benzene, recrystallized from alcohol. 2,63 g (83,7% of theoretical) of a material with m.p. of 181-182,5° was obtained. This material, which was in the form of acicular crystals, was insoluble in water, sparingly soluble in alcohol (readily in hot alcohol), and soluble in chloroform and dichloroethane.

Found %: C 35,40, 35,81; H 1,22, 1,35; N 13,53, 13,82; S 15,21, 15,63; Cl 35,01, 34,80. $C_6H_2N_2SCl_2$.
Calculated %: C 35,12; H 0,97; N 13,63; S 15,63; Cl 34,63.

b) The remaining three isomers were synthesized from the corresponding dichloro-o-diamines and thionylaniline in a manner similar to the preceding.

Bromination of benzo-2,1,3-thiadiazole. 32 g of bromine was added with constant stirring over a period of 25 minutes to 9 g of melted piazothiole, m.p. 42°, after which the reaction mixture was heated to boiling for an hour; the solid mass, which formed on cooling, was allowed to stand in air until the excess bromine evaporated. 28,85 g (95,55% of theoretical) of a yellow substance was obtained; recrystallization from alcohol gave white crystals, m.p. 142°, which were readily soluble in benzene, carbon tetrachloride, acetone, and acetic acid and less soluble in alcohol.

Found %: N 6,19, 6,20. $C_6H_4N_2Br_4S$. Calculated %: N 6,14.

4,7-Dibromobenzo-2,1,3-thiadiazole. a) 1 g of tetrabromotetrahydrobenzo-2,1,3-thiadiazole, m.p. 142°, 20 ml of alcohol, and a solution of 0,32 g of potassium hydroxide in 1 ml of water were heated to boiling for 1 hour; after cooling and dilution with water, there was obtained 0,42 g (65% of theoretical) of a substance which, after recrystallization from alcohol, melted at 184-185°. A mixed sample with 4,7-dibromobenzo-2,1,3-thiadiazole melted without depression of the melting point.

b) Synthesis of 4,7-dibromobenzo-2,1,3-thiadiazole. 1 g of 3,6-dibromo-1,2-diaminobenzene, m.p. 92-94°, 1,2 g of thionylaniline, b.p. 198-200°, and 3 ml of benzene were heated to boiling for 30 minutes. After cooling, the resulting precipitate was filtered, washed with benzene, and recrystallized from alcohol. There was obtained 1 g of 4,7-dibromobenzo-2,1,3-thiadiazole, m.p. 184-185°.

Found %: N 9,68, 9,61. $C_6H_2Br_2N_2S$. Calculated %: N 9,52.

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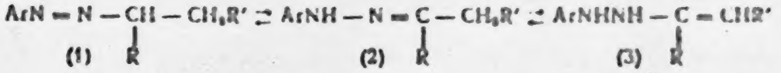
ON THE MECHANISM OF THE FISCHER REACTION AND ITS ANOMALIES

Academician A. E. Arbuzov and Yu. P. Kitaev

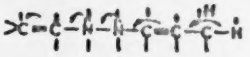
Earlier [5] we have shown that arylhydrazones can exist in three tautomeric forms:



$$\underset{(1)}{ArN=N-\underset{R}{\underset{|}{CH}}-CH_2R'} \rightleftarrows \underset{(2)}{ArNH-N=\underset{R}{\underset{|}{C}}-CH_2R'} \rightleftarrows \underset{(3)}{ArNHNH-\underset{R}{\underset{|}{C}}=CHR'}$$

The polarographic activity of all these forms is evidence of bond conjugation in their molecules. We shall now elucidate the nature of the interaction of the bonds in the enhydrazine form [1-4].

Molecules of compounds having the enhydrazine structure contain a system of two double bonds separated by two nitrogen atoms, i.e., there are present two groups, each of which is πp-conjugated. The free electron pairs on the nitrogen atoms act upon one another and upon the N–N bond, linking the πp-groups into a πppπ-conjugated system. The bond activation energy of this system is approximately 15 kcal/mole less than in the πpπ-system in hydrazines, and 33.0 kcal/mole less than in the ππ-system of azo-compounds [5]. As one of the double bonds enters the aromatic nucleus the symmetry of the system is disturbed, the polarization of the chain is displaced toward the left and alkyl substituents on No. 6-atom will act in the same direction (conjugation C=C–C–H.



In this conjugated chain No. 1 and No. 6 carbon atoms are most reactive.

In the case of compounds of the enhydrazine type, bond conjugation is characterized by a considerable exaltation of molecular refraction (see Table 1).

TABLE 1

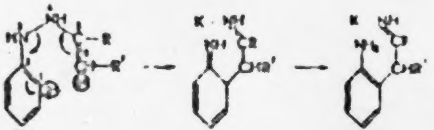
Compound	Mol. wt.	n_D^{20}	d_4^{20}	MR found	MR calc.	$\Delta MR = MR_f - MR_c$
$C_6H_5NHNH-\overset{CH_3}{\overset{\vert}{C}}=CH_2$	148.20	1.5880	1.0144	49.152	46.682	2.470
$C_6H_5NHNH-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_3$	162.22	1.5718	1.0034	53.333	51.300	2.033
$C_6H_5NHNH-\overset{CH_3}{\overset{\vert}{C}}=C(CH_3)_2$	176.35	1.5620	0.97514	58.779	55.918	2.861

Inasmuch as arylhydrazones are basic substances they will be affected most in acid media. Thus, in the case of a hydrazone having the structure (2) there will take place, in acid medium, 1,4-addition of the acid to the πn-conjugated system:

As a result, there will be formed the more strongly basic enhydrazine. The latter, by adding a proton onto the more nucleophilic nitrogen atom, will change into an anion whose ethylenic linkage will be strongly polarized, i.e., dienophile. The -NH-NH$_2$- linkage, likewise, becomes polarized. An effect of this nature leads to the formation of a complex. On heating to a temperature above the melting point hydrazones can, apparently, also be transformed into enhydrazines.

On the basis of the above considerations we can now understand the action of catalysts in the Fischer reaction, such as acid reagents, metals and their salts which are capable of forming complexes [8-10]. All these reagents displace the tautomeric equilibrium to the enhydrazine side and bring about the activation of the bonds.

The most characteristic property of 1-4-conjugated systems is their ability to enter into reactions of the diene synthesis type [1,2]. We consider that under defined conditions certain 1-6 (and apparently also 1-8 and 1-10) conjugated systems can undergo a redistribution of the electron densities leading to an intramolecular transformation of the type of the diene synthesis. To such systems belong, to a certain extent, enhydrazine systems in which carbon atoms Nos. 1 and 6 receive some excess charges of opposite sign. If we take into account that these atoms are situated close to each other in space, we may take it as highly probable that they will be mutually attracted and will interact according to the scheme:



(I) (II) (III)

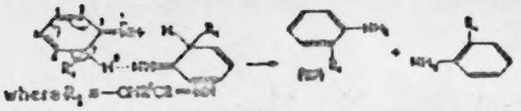
The analogy between this transformation and the diene synthesis is complete. Atoms 1,2,3 and 4 form a diene system; the 1-2 double bond is conjugated with the free electrons on No. and No. 4 atoms – a case of πpp-conjugation, resembling in many respects a ππ-conjugation; and this conjugation becomes reinforced by the action of the catalyst. The dienophile nature of the 5-6 bonds has already been discussed. Diene synthesis reactions are characterized by the appearance of a double bond between Nos. 2 and 3 carbon atoms, and of new bonds between the atoms of the dienophile and the No. 1 and No. 4 atoms of the diene as the 1-2 and 3-4 bonds are ruptured. All these processes are expressed in the scheme given above which constitutes the first step in the Fischer reaction. Further transformation of the intermediate o-(β-iminoalkyl)-aniline which can sometimes be isolated [11,12], gives indole according to the scheme put forward by Robinson and Robinson [13] and supplemented by Allen and Wilson [14].

The generalized theory of conjugation has thus made it possible to reveal the "motive power" behind the transformation taking place in the Fischer reaction and to define more accurately the reaction mechanism.

A scheme similar to our own put forward by Carline and Wallace in 1948 who took as their starting point the "formal analogy" between the first step of this reaction and the Claisen rearrangement. We consider, however, that here the analogy is not a formal, but a fundamental one, since in both cases there is transformation of 1-6-conjugated systems.

The mechanism given above for the Fischer reaction which follows from the generalized theory of conjugation and applies also to the Brunner – Piloty reaction [10], is in agreement with all experimental facts and, to some extent, with the observations of V. V. Feofilaktov [16]:

As a result of σππ-conjugation hydrogen atom No. 8 in the molecule of the intermediate o-iminoquinone (II) becomes labile while the electron density on the nitrogen atom increases. Orientation and closer approach of the molecules lead to a redistribution of electrons and formation of aniline (III):



A similar mechanism is, apparently, followed also by certain tautomeric transformations. The formation of 5,7-dichlorindoles from 2,6-dichlorophenylhydrazones [17] can also be explained by means of this mechanism.

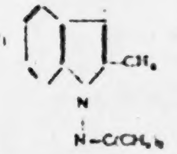
One of us, having at one time demonstrated the catalytic nature of the Fischer reaction [18], found that if cuprous chloride is used as the catalyst, aldehyde arylhydrazones will yield, in addition to indole (or even exclusively), the nitrile corresponding to the acid from which the aldehyde is derived, and aniline. Acetone phenylhydrazone will give, in the presence of Cu_2Cl_2, a complex substance, ammonia and aniline [19]:

$$2C_9H_{12}N_2 \rightarrow C_{12}H_{14}N_2 + C_6H_5NH_2 + NH_3$$

It has been suggested that arylhydrazones of ketones which do not contain a methylene group adjacent to the carbonyl group, should also be decomposed by Cu_2Cl_2 according to the anomalous mechanism.

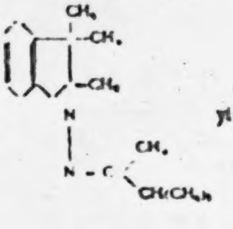
In the present investigation it has been shown that such a suggestion is, indeed, justified as exemplified by phenylhydrazones of acetone, methyl isopropyl ketone, pinacoline, pyrotartaric acid, acetophenone, p-chloracetophenone, as well as acetone methylphenylhydrazones. The amount of ammonia evolved during the reaction was always less than the required by the equation for the normal reaction, and was much closer to the amount corresponding to the equation for the anomalous reaction. From the phenylhydrazones of acetone and methyl isopropyl ketone there were obtained abnormal products of reaction for which structures (IV) and (V) have been proposed. These substances easily undergo change on exposure to air.

(IV)



b.p. 138 – 139° 10 mm
n_D^{20} 1.5801
d_{20}^{4} 1.0520
yield 21 %

(V)



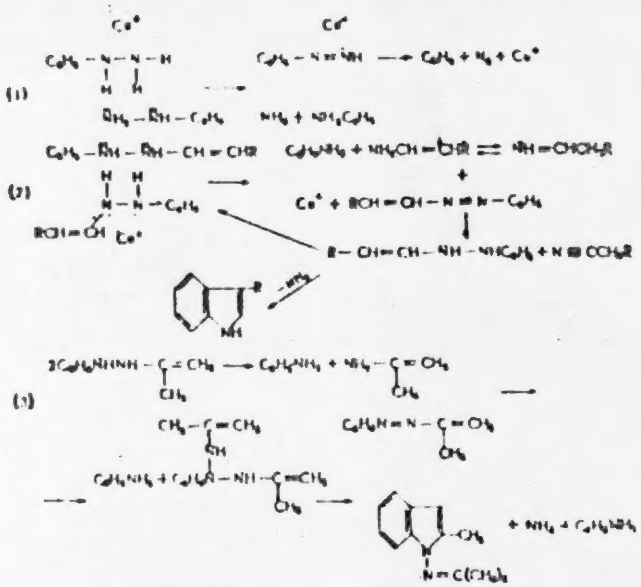
b.p. 144 – 148°/10 mm
yield . 12 %

In the remaining cases there were obtained aniline, ammonia and tars which could not be purified, while in the case of the methylphenylhydrazone, only tarring occurred.

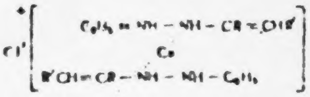
We consider that the formation of nitriles and N-substituted indoles from arylhydrazones as well as the decomposition of phenylhydrazine in the presence of a catalyst [20,21] are processes related by their reaction mechanism, and we propose the following schemes for these reactions [see (1-3) on following page].

In these schemes it is assumed that the hydrazine entering into the complex reduces the free base. This mechanism is in agreement with the observations of Clusius [21] who decomposed phenylhydrazine labelled with the N^{15} isotope.

The disproportionation of hydrazobenzene [22], the formation of osazones [23] and the interaction of azobenzene with phenylhydrazine [24] also follow a similar mechanism, and since these reactions take place without the aid of catalyst it follows that free hydrazines also can reduce molecules akin to themselves.



The anomalous Fischer reaction evidently also takes place when the catalyst forms coordinate links with both nitrogen atoms of hydrazine, for example:



$$\mathrm{Cl}^{-}\left[\begin{array}{c} C_6H_5-NH-NH-CR=CHR' \\ Cu \\ R'CH=CR-NH-NH-C_6H_5 \end{array}\right]^{+}$$

It is, however, still not clear why not all arylhydrazones undergo the anomalous reaction. We have found that sulfanilic acid is also a good catalyst of this reaction. The action of this acid derives, apparently, from its ability to form hydrogen bonds with hydrazines and to enhance the nucleophilic character of the nitrogen atoms, i.e., its action runs counter to that of cuprous salts. In this case the free base is the reducing agent.

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ON THE COMPOUND Ni_3B IN NICKEL-BORON ALLOYS

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(Presented by Academician S. I. Vol'fkovich, Nov. 30, 1956)

The binary diagram for the system Ni-B (up to 20% B) was first constructed by Giebelhausen in 1915 [1]. Giebelhausen found that in the system Ni-B the compound richest in nickel is Ni_2B. Binet du Jassonneix [2] isolated this compound from alloys containing 5% B. Bjurström [3] in the course of x-ray structural investigation of the Ni-B alloy established that the phase Ni_2B (8.46%) is isomorphous with the phases Fe_2B and Co_2B and that it has a tetragonal space-centered crystal lattice with the parameters: $a = 4.980$ kX, $c = 4.236$ kX. On the basis of results of x-ray investigations Kiessling [4] stated that nickel-rich alloys contain, in addition to the phase Ni_2B, a phase Ni_3B, but did not give its characteristics.

We have carried out an investigation of the structure and phase composition of Ni-B alloys containing from 0.01 to 2.5% B. The alloys were cast, an NiB alloy containing 5% B being introduced into the melt.

Metallographic investigation of the cast alloys revealed that along the grain boundaries there was formed a uniformly etched phase which constituted a eutectic mixture with nickel. The alloy with 2.5% B is pre-eutectic (Fig. 1). We have succeeded in isolating this phase both chemically and by electrolysis. In order to isolate it by chemical means a small amount of chips of the alloy was heated with sulfuric acid (1 : 2) until no more of the solid dissolved.

TABLE 1

Content of Ni and B in the Insoluble Residue Obtained After Heating the Alloy with H_2SO_4 (1 : 2) Until Dissolution Ceased

% B in alloy	% in insoluble residue		Atomic ratio, Ni : B
	Ni	B	
0.19	1.48	0.085	3.2 : 1
0.34	2.48	0.17	2.8 : 1
1.62	13.8	0.78	3.3 : 1
2.27	20.0	1.19	3.1 : 1
2.49	20.8	1.30	3.0 : 1

The phase isolated by either method was examined for structure by x-rays and analyzed chemically.

Figure 2 shows a typical x-ray diffraction diagram of the isolated phases photographed in CuK_α-radiation. Below are given the results of x-ray structural analysis of the phase Ni_3B, carried out by the powder method.

In the electrolytic method of separation of the phases a cylindrical sample of the alloy was employed as anode under the usual conditions, using an aqueous and a nonaqueous electrolyte of the following compositions: (1) 10 g of $(NH_4)_2SO_4$, 30 g of hydroxylamine hydrochloride per 1200 ml of water, and (2) 50 ml of HCl per 1150 ml of methanol, with cooling.

TABLE 2

Content of Ni and B in Anodic Residues Deposited Electrolytically in Aqueous Electrolytes

% B in alloy	Electrolyte	% in anode residue		Atomic ratio, Ni : B
		Ni	B	
2.49	1	5.80	0.40	2.7 : 1
2.49	2	10.63	0.63	3.2 : 1
2.49	3	11.80	0.80	2.7 : 1

Note. Electrolyte composition: 1) 10 g of $(NH_4)_2SO_4$, 35 g of citric acid, 15 g of NH_2OH; 2) 10 g of $(NH_4)_2SO_4$, 35 g of citric acid, 25 g of NH_2OH, 1200 ml of water; 3) 10 g of $(NH_4)_2SO_4$, 30 g of NH_2OH, 1200 ml of water, with cooling.

No.	Intensity	d, in A	No.	Intensity	d, in A
1	m	2.43	21	s-m	1.226
2	s	2.35	22	m-s	1.187
3	m	2.25	23	s	1.159
4	s-m	2.12	24	m	1.139
5	v-m	2.035	25	s	1.123
6	s	1.98	26	m	1.108
7	s	1.94	27	m-w	1.076
8	vs	1.85	28	v-w	1.032
9	s-m	1.74	29	w	1.001
10	m	1.68	30	vs	0.9679
11	vw	1.64	31	vw	0.2500
12	m	1.62	32	w	0.9293
13	w-s	1.57	33	m	0.9242
14	w-s	1.44	34	w	0.8632
15	w	1.40	35	s	0.8551
16	w	1.38	36	w	0.8413
17	w	1.335	37	s	0.8274
18	s	1.294	38	s-m	0.8240
19	s-m	1.250	39	s	0.8163
20	w	1.232	40	s-m	0.8041

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* Significance of abbreviations: m = medium, s = strong, w = weak, vs = very strong, vw = very weak.

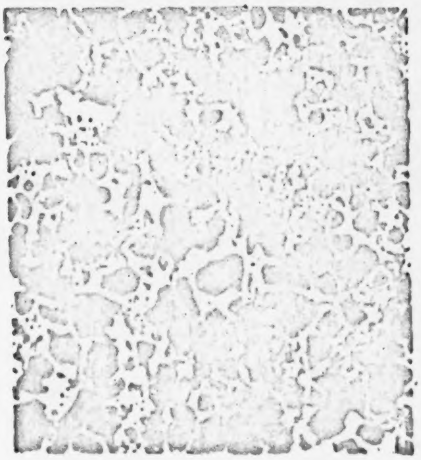

Fig. 1

TABLE 3

Content of Ni and B in Anodic Deposits Formed in Non-aqueous Electrolyte (50 ml of HCl (1.19) per 1150 ml of CH_3OH), With Strong Cooling

% in alloy	% in insoluble residue		Atomic ratio,
	Ni	B	Ni : B
0.19	0.077	0.005	2.7 : 1
0.34	0.230	0.018	2.8 : 1
2.49	0.96	0.066	2.7 : 1

The results of chemical analysis of the phases isolated from the alloy by the different methods are shown in Tables 1-3, and are based on the weight of the alloy dissolved.

Fig. 2.

From the data given in Tables 1-3 it will be seen that in the course of the electrolytic separation of the phases a considerable proportion of the nickel boride goes into solution, while in the treatment with sulfuric acid (1 : 2) most of it remains undissolved. Data from the x-ray examination show that in all cases the anodic deposit constituted one and the same phase. In accordance with the results of chemical analysis the composition of the deposited phase may be represented by Ni_3B.

This nickel boride has the appearance of a black solid. It is insoluble in dilute sulfuric acid (1:2). It dissolves in concentrated sulfuric acid (1.84) on prolonged heating. It hardly dissolves in concentrated (1.19) or in dilute hydrochloric acid (1:1) even after prolonged heating. It dissolves in the cold in dilute nitric acid and in aqua regia. It also dissolves easily in dilute hydrochloric and sulfuric acids in the presence of oxidizing agents such as hydrogen peroxide, potassium persulfate, etc.

On the basis of these investigations it can, therefore, be stated that the system Ni-B includes the chemical compound Ni_3B which forms a solid-solution eutectic mixture on nickel as base.

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RUPTURE OF THE PYRAZOLINE RING DURING ACYLATION

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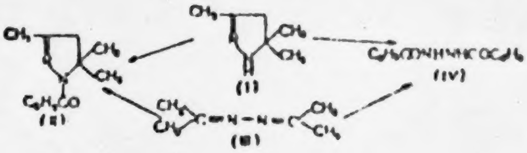
Pyrazolines which have no substituent on the nitrogen atom, may be transformed into the corresponding N-acylpyrazolines by the action of acid anhydrides or acid chlorides [1,2]. However, it has been observed that anomalies sometimes occur in the acylation of pyrazolines. Thus, Fraundenberg and Stoll [3], while benzoylating 5-methyl-3-phenylpyrazoline, obtained, instead of 1-benzoyl-5-methyl-3-phenylpyrazoline, a substance having m.p. 214° whose structure they did not investigate. While benzoylating 2,5,5-trimethylpyrazoline (I) according to Schotten-Baumann we have isolated two substances. One of these (A) had m.p. 236° and was soluble in aqueous alkali; the other substance (B) had m.p. 93° and was insoluble in alkalies.

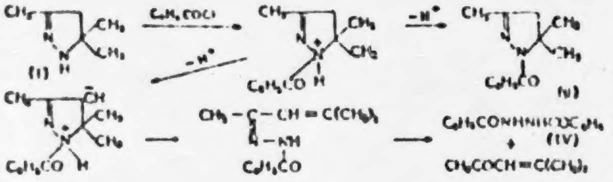
Curtius and Wirsing [illegible] Frey and Hofmann [5], in the course of reacting benzoyl chloride with the pyrazoline in question (I), obtained a substance A which they described as 1-benzoyl-3,5,5-trimethylpyrazoline (II). In 1928 Lochte and co-workers [6] reported that benzoylpyrazoline (II), having m.p. 236°, was formed during cyclization of acetoneazine (III) by the action of benzoyl chloride. However, the substance A (m.p. 236°) which was taken by the above authors to be benzoylpyrazoline (II), proved to be N,N'-dibenzoylhydrazine (IV) as was shown in our experiments, the results of which were confirmed by synthesis and by a comparison of the corresponding absorption spectra. Substance B (m.p. 93°) which has not been isolated by the above authors, proved to be the benzoylpyrazoline (II) sought.

It has been found that, depending on its conditions, the reaction between benzoyl chloride and pyrazoline (I) can be made to proceed either to complete rupture of the pyrazoline ring with the formation of dibenzoylhydrazine (IV), or in the direction of normal benzoylation. When pyrazoline is added to excess benzoyl chloride in the presence of aqueous alkali, dibenzoylhydrazine (IV) is obtained as the sole product of reaction. When the reactants are added in the reverse order, or if the reaction is carried out under complete exclusion of moisture, only benzoylpyrazoline (II) is formed. It is interesting to note that with acetoneazine (III) the reaction follows a similar pattern, giving exclusively benzoylpyrazoline (II) in anhydrous media, while in the presence of moisture and excess benzoyl chloride the azine is decomposed with the formation of dibenzoylhydrazine (IV).



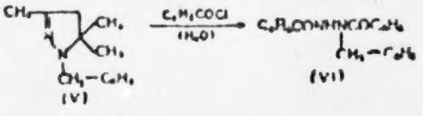
During the decomposition of acetoneazine (III) there was formed, in addition to dibenzoylhydrazine (IV), acetone which was identified in the form of its semicarbazone, while in the case of the pyrazoline I there was similarly obtained mesityl oxide which was also transformed into its semicarbazone.

The ability of pyrazolines to undergo the cleavage of the C–N bond with comparative ease resembles the corresponding properties of their structural analogs – the β-aminoketones; in the latter case the mechanism of the splitting off of the amino group has been the subject of systematic investigation [7]. In the presence of a constant excess of free pyrazoline, or under anhydrous conditions, hydrogen chloride is split off and acylation takes place. In the presence of hydroxyl ions (in aqueous alkaline medium) and excess benzoyl chloride a proton is split off at position 4, followed by opening of the ring.



Formation of dibenzoylhydrazine (IV) was also observed to take place during benzoylation of 4-ethyl-5-propylpyrazoline. This action of benzoyl chloride does not appear to be specific of this acylating agent. Thus, by the action of caproyl chloride on pyrazoline (I), or on 3-methyl-5-phenylpyrazoline, there was obtained symmetrical dicaproylhydrazine.

Benzoylpyrazoline (II) resists the action of benzoyl chloride (under various conditions), but 1-benzyl-3,5,5-trimethylpyrazoline (V) decomposes fairly easily giving N,N'-dibenzoylbenzylhydrazine (VI).



Pyrazolines are acylated by acid anhydrides without rupture of the ring, although, as is well known [8], acid anhydrides can decompose azines.

EXPERIMENTAL

1-Benzoyl-3,5,5-trimethylpyrazoline (II). To a solution of 45,4 g (0,2 mole) of benzoic anhydride in 50 ml of anhydrous benzene was added 11,2 g (0,1 mole) of 3,5,5-trimethylpyrazoline (I). The benzene solution was washed with 2N sodium hydroxide, dried, the solvent removed and the residue recrystallized from absolute alcohol. Yield 18,7 g (83% of theory), m. p. 92,5-93°.

Found %: C 72,25, 72,37; H 7,57, 7,65. $C_{13}H_{16}ON_2$. Calculated %: C 72,19; H 7,45.

The absorption spectrum in methyl alcohol has λ_{max} = 247 mμ and log ε = 4,348.

Interaction of 3,5,5-trimethylpyrazoline (I) with benzoyl chloride. To a mixture of 11,2 g (0,1 mole) of pyrazoline (I) and 50 ml of 2N sodium hydroxide was added, dropwise, 16 g (0,12 mole) of benzoyl chloride. After shaking for 10 minutes there formed a white mass which gradually crystallized. The crystals were washed repeatedly with cold 2N sodium hydroxide solution and with hot water and were then treated with 100 ml of 40% sodium hydroxide. The residue was recrystallized from absolute alcohol. Yield of 1-benzoyl-3,5,5-trimethylpyrazoline, 6,4 g (29,6% of theory), m.p. 92-92,5°. There was no depression of melting point with 1-benzoyl-3,5,5-trimethylpyrazoline. On neutralizing the alkaline extract there was obtained 3,3 g (22,4% of theory) of 1,2-dibenzoylhydrazine (IV). M. p. 234-236°. Literature [9], m.p. 236°. No depression of melting point was observed with a known sample of 1,2-dibenzoylhydrazine. The absorption spectrum in methyl alcohol has λ_{max} = 232 mμ and log ε = 4,279.

When 11 g of pyrazoline (I) was added slowly to a well-shaken mixture of 14 g (0,1 mole) of benzoylchloride, 25 ml of benzene and 7 g of moist soda crystals, followed by similar treatment, 1,2-dibenzoylhydrazine was obtained as the only product of reaction. Yield, 11,8 g (97% of theory), m.p. 236°. When benzoyl chloride was added to pyrazoline (I) under the same conditions, in the presence of benzene and moist soda, only 1-benzoyl-3,5,5-trimethylpyrazoline formed in yield of 67,5% of theory. M.p. 92,5-93°. When the reaction between benzoyl chloride chloride and 3,5,5-trimethylpyrazoline is carried out under anhydrous conditions followed by frac-

145-149° (4 mm), m. p. 93-93°. In this case the order of addition of the starting materials is not important. Mesityl oxide semicarbazone was obtained by treating the ether extracts of the washings obtained from the fractionation of pyrazoline, with semicarbazide. M. p. 162°. Literature [10], m. p. 163-164°.

Interaction of 4-ethyl-5-propylpyrazoline with benzoyl chloride. To 7 g (0.05 mole) of 4-ethyl-5-propylpyrazoline [11] (b.p. 110-112° at 22 mm; n_D^{23} 1.4682, d_4^{23} 0.9130; MR_D 42.71 calcd. for $C_8H_{16}N_2$, 42.81) was added, in the presence of 5 g of soda, 9 g (0.07 mole) of benzoyl chloride. The separated oil was washed free from benzoic acid and distilled twice in vacuo. There was obtained 6.9 g (49.3% of theory) of 1-benzoyl-4-ethyl-5-propylpyrazoline, m.p. 180-181° (10 mm); n_D^{20} 1.5689; d_4^{20} 1.0357; MR_D 71.18; calcd. $C_{15}H_{20}ON_2$, 71.62.

Found %: N 12.83, 12.65. $C_{15}H_{20}ON_2$. Calculated %: N 12.45.

If pyrazoline is added to the reaction mixture, 1,2-dibenzoylhydrazine is formed. Yield 21% of theory.

Interaction of 3,5,5-trimethylpyrazoline with caproyl chloride. 5.6 g (0.05 mole) of pyrazoline (I) was added to 7 g (0.05 mole) of caproyl chloride in the presence of 5 g of moist soda. After the usual treatment 1,2-dicaproylhydrazine separated. Yield, 4.6 g (80.6%), m.p. 159° (from alcohol). Literature [12], m.p. 159°. There was no depression of melting point with an authentic sample of 1,2 dicaproylhydrazine [12].

Interaction of 3-methyl-5-phenylpyrazoline with caproyl chloride. When the reaction was carried out under similar conditions with 14 g (0.1 mole) of caproyl chloride and 16 g (0.1 mole) of 3-methyl-5-phenylpyrazoline, there was obtained 7.1 g (62% of theory) of dicaproylhydrazine, m.p. 159°.

Interaction of 1-benzyl-3,5,5-trimethylpyrazoline (V) with benzoyl chloride. A mixture of 11.2 g (0.08 mole) of benzoyl chloride, 7.4 g (0.036 mole) of pyrazoline (V) and 4.5 g of soda crystals was heated to boiling and, after cooling, treated in the usual way. Yield of N,N'-dibenzoylbenzylhydrazine, 1.9 g (16% of theory), m.p. 148° (from alcohol). Literature [13], m.p. 148°. No depression of melting point with a known sample of N,N'-dibenzoylbenzylhydrazine [13] was observed.

Interaction of acetoneazine (III) with benzoyl chloride. To 14 g (0.1 mole) of benzoyl chloride was added slowly a solution of 11.2 g of acetoneazine in 25 ml of benzene. To the reaction mixture was added 30 ml of water, and after the usual treatment there separated dibenzoylhydrazine (IV). Yield 17.3 g (72.5% of theory), m.p. 235-236°. If the reaction mixture was immediately fractionated in vacuo, benzoylpyrazoline (II) was obtained. Yield 2.7 g (12.4% of theory), b.p. 146-147° (4 mm), m.p. 92-93°. From the aqueous washings obtained from the decomposition of the azine, there was obtained by the action of semicarbazide, acetone semicarbazone. M.p. 185-186°. Literature [14], m.p. 187°.

1-propionyl-3,5,5-trimethylpyrazoline. 10.6 g (0.1 mole) of propionyl chloride was added dropwise to 11.2 g (0.1 mole) of pyrazoline (I) in the presence of 5 g of soda crystals. The reaction mixture was washed with 2N sodium hydroxide and extracted with ether. After fractionation there was obtained 7.2 g (43%) of 1-propionyl-3,5,5-trimethylpyrazoline, b.p. 125-127° (21 mm), n_D^{20} 1.4779; d_4^{20} 0.9813; MR_D 48.39; MR_D calcd. for $C_9H_{16}ON_2$, 48.60.

Found %: N 16.93, 16.97. $C_9H_{16}ON_2$. Calculated %: N 16.66.

1-Butyryl-3,5,5-trimethylpyrazoline was obtained from 11.2 g (0.1 mole) of pyrazoline (I) and 11 g (0.1 mole) of butyryl chloride in a manner similar to that described above. Yield 8.3 g (45.7%), b.p. 121-123° (13 mm); n_D^{20} 1.4665, d_4^{20} 0.9663; MR_D 52.22; MR_D calcd. for $C_{10}H_{18}ON_2$ 52.43.

Found %: C 66.75, 66.76; H 10.04, 10.11. $C_{10}H_{18}ON_2$. Calculated %: C 66.44; H 9.95.

1-Isovaleryl-3,5,5-trimethylpyrazoline was obtained in a similar manner from 4.5 g (0.04 mole) of pyrazoline (I) and 7.2 g (0.06 mole) of isovaleryl chloride in 25 ml of benzene. Yield 3.3 g (42.5%), b.p. 108-110° (10 mm); n_D^{20} 1.4712; d_4^{20} 0.9520; MR_D 57.65; calcd. for $C_{11}H_{20}ON_2$, 57.84.

Found %: N 14.45, 14.33. $C_{11}H_{20}ON_2$. Calculated %: N 14.27.

1-(m-Nitrobenzoyl)-3,5,5-trimethylpyrazoline. This was obtained similarly, from 4.5 g (0.04 mole) of pyrazoline (I) and 8 g (0.05 mole) of m-nitrobenzoyl chloride, as a viscous oil which crystallized on standing. Yield 5.2 g (72.3%), m.p. 99.5-100° (from alcohol).

Found %: N 16.24, 16.34. $C_{13}H_{15}O_3N_3$. Calculated %: N 16.09.

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** Russian translation.

ON THE THERMAL STABILITY OF COMPLEXES OF UREA WITH ORGANIC COMPOUNDS

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(Presented by Academician A. N. Frumkin, November 28, 1956)

Urea forms crystalline complexes with almost all types of straight-chain organic compounds – hydrocarbons, ethers, aldehydes, acids, alcohols, etc. [1,2].

Among investigators occupied with questions of the formation and stability of complexes of urea with organic compounds, the idea has become established that urea cannot form complexes above its melting point. (132.7°) [3-6]. Although up to the present time no urea complexes stable above 132.7° have been observed, nevertheless it is completely incomprehensible, from the point of view of thermodynamics, why the melting point of urea should be an upper limit for the existance of a complex. At temperatures below 132.7°, complexes in equilibrium with urea in unsaturated solutions (aqueous solutions, for example) have been observed [7]. Urea in unsaturated solutions, particularly aqueous solutions which are nearly ideal solutions, is properly considered from the thermodynamic point of view as liquid urea with an activity less than that of solid urea at the same temperature.

The thermal stability of a complex is greater the longer the chain of the organic compound [2,7]. The thermal stability of a complex prepared from a mixture of organic substances is greater than the thermal stability of the complexes prepared from the individual components of the mixture [7]. Therefore, in the search for complexes stable above the melting point of urea, the authors conducted experiments with paraffin and with ceresin, i.e., with multicomponent mixtures consisting mainly of long-chain hydrocarbons of the paraffin series.

Chemically pure urea, commercial paraffin with a molecular weight of 307 and m.p. of 41-43°, and various types of purified ceresins were used for the experiments. The synthetic ceresin had m.p. of 82-83°.

The complexes of urea with paraffin or ceresin were synthesized in sealed glass tubes having a volume of 1.5-2.5 cc. The formation of complexes of urea with paraffin or ceresin began only at temperatures above the melting point of paraffin or ceresin. The reaction between urea and ceresin proceeded very slowly over a period of several hours. The most favorable condition for the formation of the complex was slow cooling of the molten mixture of urea and ceresin.

The glass tube containing the complex was fastened in a rack in a thermostated air bath with windows [illegible]. The temperature in the bath was raised slowly, and the temperature of complete disappearance of the complex was observed visually.

Organic component	Temperature, °C
Paraffin	124.5
Ceresin from Surakhansk formation	134.0
" " Shor-Su formation	135.0
" " Borislav formation	137.5
" synthetic No. 1	140.0
" " No. 2	140.5
" " No. 3	141.0

The complexes of urea with the different types of ceresin were stable above the melting point of urea. The complex of urea with synthetic ceresin No. 3 existed at a temperature of 141.0°.

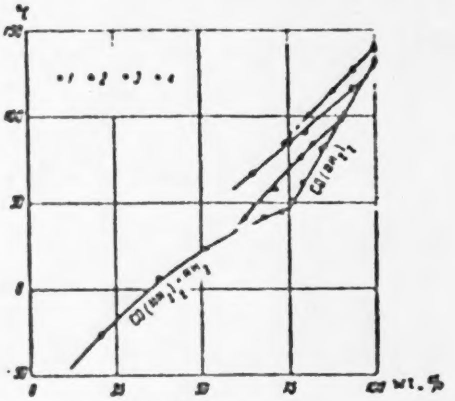

Fig. 1. Thermal stability of complexes of urea with cetane, paraffin, and ceresin in liquid ammonia: 1) solubility of urea in liquid ammonia, 2) urea-cetane complex, 3) urea-paraffin complex, 4) urea-ceresin complex.

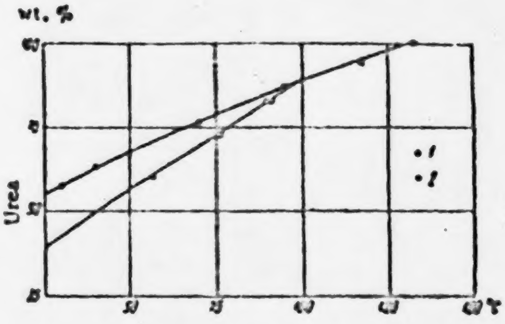

Fig. 2. Thermal stability of urea-cetane complex in aqueous solution: 1) solubility of urea in water, 2) thermal stability of the complex.

In order to confirm the stability of the equilibrium between the complex and the molten urea, a sealed tube containing the complex of urea with synthetic ceresin No. 3 was rotated in the air bath for ten hours at 136°. The complex did not decompose, and in the melt of urea and ceresin floated the complex precipitate. There was only a clear urea melt in a control tube containing urea alone.

The stability of the complex at temperatures above the melting point of urea can be demonstrated by another method by studying the equilibrium between the complex and urea in unsaturated urea solutions.

It is well known that in aqueous solutions of urea, the stability of the complex depends on the urea concentration of the solution [7]. It is evident that the curve of the temperature stability of a complex begins at a temperature below the melting point of urea, and ends at the temperature above which the complex cannot exist regardless of the urea concentration of the solution. Therefore, in order to determine the stability of complexes at temperatures above the melting point of urea, it is necessary to trace the course of the temperature curve. Water was not suitable as a solvent for these experiments, since the reaction between urea and water to give ammonia and carbon dioxide proceeds at an appreciable rate above 100° [9]. Liquid ammonia was selected as the solvent.

The authors measured the solubility of urea in liquid ammonia by the synthetic method of Alekseev [10], and obtained good agreement with literature data [11] (Figure 1). The solubility curve for urea in liquid ammonia has a break at 46° – the melting point of the compound $CO(NH_2)_2 \cdot NH_3$.

As in the experiments without a solvent, the complex was synthesized in a sealed, heavy-wall tube, the tube was rotated in the bath, and, while raising the temperature slowly, the temperature at which the complex completely disappeared was determined visually (Figure 1).

The temperature-stability curve for the urea-paraffin complex ends at 124.5°, but the temperature curve for the urea-ceresin complex clearly extends above melting point of urea and is directed toward the previously determined temperature of 141.0° (see above).

In order to determine the accuracy of the method used, the authors measured the thermal stability of the urea-cetane complex in aqueous urea solutions (Figure 2), and obtained good agreement with the literature data [7]. The temperature-stability curve of the complex crosses the curve of the solubility of urea in water at 96° (Figure 2).

During the investigation of the thermal stability of the urea-cetane complex in ammonia solutions of urea, we observed that the solubility curve for the urea intersects the thermal stability curve of the complex at a somewhat higher temperature, 99° (see Figure 1). This discrepancy can be explained by partial decomposition of the urea in aqueous solutions during lengthy experiments (several hours), owing to which the actual concentration of urea in the aqueous solution was somewhat less than the value assigned.

The thermal stability curve for the urea-cetane complex intersects both branches of the solubility curve for urea in liquid ammonia (see Figure 1), and the complex is stable within this temperature interval.

Several qualitative observations on conditions for the formation of complexes were made while carrying out the experiments for measuring the thermal stability of the complexes.

In experiments with unsaturated solutions of urea in liquid ammonia, if, after the temperature was reached at which the complex of urea with cetane (paraffin, ceresin) completely decomposed, the temperature was decreased 5-10°, the complex did not form again even after rotating many hours in the bath. Formation of the complex required cooling by 15-25° and, in some experiments, by 40-45°. If the complex was not completely decomposed during the temperature rise, leaving a small amount of "seed" remaining, the amount of complex did not increase on cooling while rotating the tube in the bath for several hours. If the complex was decomposed at the temperature at which the solubility and stability curves intersect, lowering the temperature by 10-15° not only did not form complex, but did not precipitate urea from its supersaturated solution. In the control sealed tube containing no cetane (paraffin, ceresin), crystallization began on supercooling the solution 1-1.5°.

The reason for the delay in crystallization of complex can be found in the small probability of forming nuclei of complex if we take into account that in the complex of urea with cetane, for example, one molecule of cetane requires twelve molecules of urea [7]. The delay in the crystallization of urea in the presence of cetane (paraffin, ceresin) can be explained by the adsorption of molecules of cetane (paraffin, ceresin) on the surface of urea nuclei which hinders further growth of the nuclei.

Thus, by means of urea-ceresin complexes it was shown that the melting point of urea (132.7°) is not a limit above which the complex cannot exist. The complex of urea with synthetic ceresin is stable to 141.0°.

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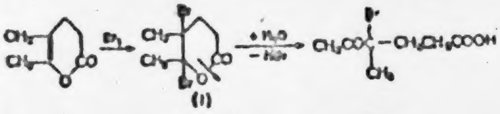
δ-LACTONES. CONVERSION OF DIBROMIDES OF UNSATURATED δ-LACTONES TO BROMO-SUBSTITUTED δ-KETO ACIDS AND THEIR ESTERS

R. Ya. Levina, N. P. Shusherina and M. Yu. Lurye

(Presented by Academician A. N. Nesmeyanov, December 3, 1956)

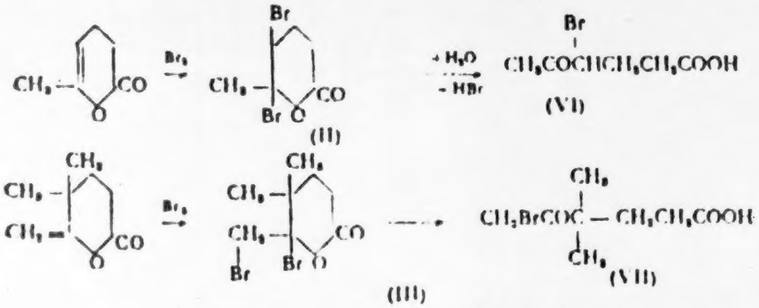
In our previous communication [1], the reaction between a dibromide of an unsaturated δ-lactone – 5,6-dibromo-5,6-dimethyltetrahydro-α-pyrone (I) – and water was described for the first time; it was shown that the reaction consists of the addition of water with cleavage of the lactone ring and the splitting out of one molecule of hydrogen bromide, and leads to the formation of γ-bromo-γ-acetylvaleric acid (in quantitative yield):

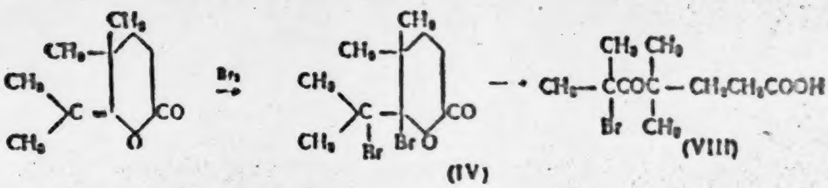

CH₃
CH₃
CO
O
Br₂
CH₃
CH₃
Br
Br
CO
O
+H₂O
−HBr
CH₃COC—CH₂CH₂COOH
Br
CH₃
(I)

The structure of the resulting bromoketo acid was proved by counter synthesis – bromination of γ-acetylvaleric acid with dioxane dibromide.

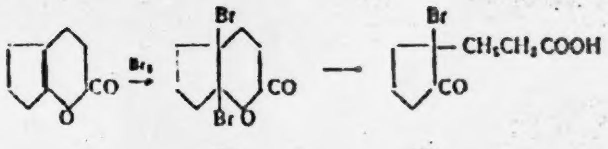
In the present work it was shown that the reaction between dibromides of unsaturated δ-lactones and water can serve as a method for the preparation of γ- or ε-bromo-substituted δ-keto acids; the reaction proceeds in the cold, is complete within 0.5-1 hour, and leads to the preparation of bromoketo acids in high yields (70-100% calculated on the original unsaturated δ-lactone).

The following acids, not described previously in the literature, were prepared by this route from the corresponding dibromolactones (II)-(V): 5-oxo-4-bromohexanoic acid [(VI) 70.0% yield]; 5-oxo-6-bromo-4,4-dimethylhexanoic acid [(VII), 87.2%]; 5-oxo-6-bromo-4,4,6-trimethylheptanoic [(VIII), quantitative yield]; and 2-bromo-2-(β-carboxyethyl)cyclopentanone [2-bromo-1-cyclopentanone-2-γ-propionic acid] [(IX), 78%];


CH₃
CO
O
Br₂
Br
CH₃
Br
O
CO
(II)
+H₂O
−HBr
Br
CH₃COCHCH₂CH₂COOH
(VI)
CH₃
CH₃
CH₃
CO
O
Br₂
CH₃
CH₃
CH₃
Br
Br
O
CO
(III)
CH₃
CH₂BrCOC — CH₂CH₂COOH
CH₃
(VII)



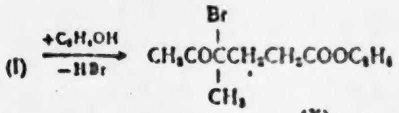
(IV) (VIII)



(V) (IX)

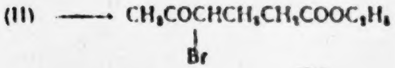
Continuing the investigation of the reactivity of dibromolactones, we were the first to study their reaction with ethyl alcohol; it was shown that in this case there proceeded the addition of alcohol with cleavage of the lactone ring and splitting out of one molecule of hydrogen bromide with the formation of ethyl esters of γ- or ε-bromo-substituted δ-keto acids* (X-XIV). The reaction proceeded with considerable evolution of heat, and was complete in half an hour; the yields of esters of bromoketo acids comprised 40-80% calculated on the original unsaturated δ-lactone.

By means of this reaction — the reaction of dibromolactones (I-V) with ethyl alcohol — we prepared the ethyl esters (X-XIV) of the above-indicated bromoketo acids (the ethyl ester XIV split out hydrogen bromide during distillation, and was converted to the ester of the unsaturated keto acid XV); these esters have not previously been described in the literature:



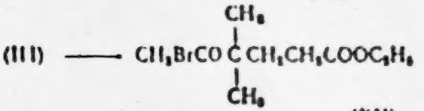
$$(I)\ \xrightarrow[-HBr]{+C_2H_5OH} CH_3CO\overset{Br}{\underset{CH_3}{C}}CH_2CH_2COOC_2H_5$$

(X)



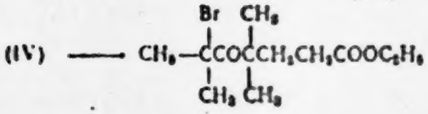
$$(II) \longrightarrow CH_3CO\underset{Br}{CH}CH_2CH_2COOC_2H_5$$

(XI)



$$(III) \longrightarrow CH_2BrCO\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2COOC_2H_5$$

(XII)



$$(IV) \longrightarrow CH_3-\overset{Br}{\underset{CH_3}{C}}CO\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2COOC_2H_5$$

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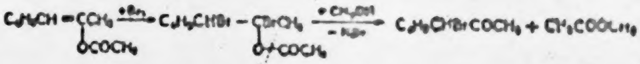
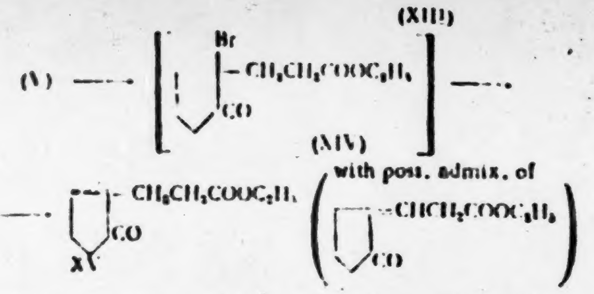
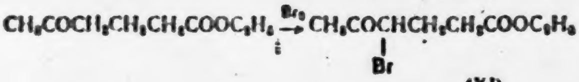
* The behavior of dibromo-δ-lactones in the reaction with alcohol recalls to a considerable extent the behavior of dibromides of vinyl esters; thus, for example, dibromides of enol acetates of ketones react with alcohols to give α-bromo-substituted ketones (3):



$$C_6H_5CH=\underset{OCOCH_3}{C}CH_3 \xrightarrow{+Br_2} C_6H_5CHBr-\underset{O-COCH_3}{CBr}CH_3 \xrightarrow[-HBr]{+CH_3OH} C_6H_5CHBrCOCH_3 + CH_3COOCH_3$$



The structure of these esters was proved by counter synthesis of one of them: ester XI was obtained by the action of dioxane bromide on the ethyl ester of γ-acetylbutyric acid:



$$CH_3COCH_2CH_2CH_2COOC_2H_5 \xrightarrow{Br_2} CH_3CO\underset{\displaystyle Br}{\underset{|}{C}H}CH_2CH_2COOC_2H_5$$

(XI)

Thus, the reaction of dibromides of unsaturated δ-lactones can serve as a method for the preparation of γ- or ε-bromo-substituted δ-keto acids and their esters.

EXPERIMENTAL

Dibromolactones. The unsaturated δ-lactones (5,6-dimethyl-3,4-dihydro-α-pyrone [1]; 6-methyl-3,4-dihydro-α-pyrone [3]; 5,5-dimethyl-6-isopropylidene-3,4-dihydro-α-pyrone [4]; 5,5-dimethyl-6-methylene-3,4-dihydro-α-pyrone [4]; and 5,6-cyclopentano-3,4-dihydro-α-pyrone [5]) were brominated in ether solution with an equimolecular amount of bromine at −10, −15°. After evaporation of the ether under vacuum in a stream of dry air, the resulting dibromides were immediately introduced into the reaction with water or ethyl alcohol, since they readily split out hydrogen bromide on standing [6].

γ- or ε-Bromo δ-keto acids. The dibromolactones (II)[*]-(V) were treated with water while stirring vigorously and cooling with ice. The reaction was complete in 0.5-1 hour. The resulting crystalline bromoketo acids were filtered and dissolved in ether; after drying the ether solutions and evaporation of the ether under vacuum, the bromo-keto acids were crystallized from petroleum ether or benzene. The melting points, yields, and analyses of the bromoketo acids are presented in Table 1.

TABLE 1

Compound	M.p., °C	Yield, %	Found, %		Calculated, %	
			C	H	C	H
5-oxo-4-bromohexanoic acid (VI) (γ-bromo-γ-acetylbutyric acid)	39—41 from petrolum ether	70	34.68 34.62	4.56 4.49	34.48	4.35
5-oxo-6-bromo-4,4-dimethylhexanoic acid (VII)	75.5—76 (from benzene)	87.2	40.71 40.70	5.45 5.50	40.53	5.65
5-oxo-6-bromo-4,4,6-trimethylheptanoic acid (VIII)	48 (from benzene)	quant.	45.32 45.40	6.35 6.50	45.27	6.40
2-bromo-2-(β-carboxyethyl)-cyclopentanone (IX)	55—56 (from a mixture of ether and petroleum ether)	78	40.74 40.88	4.85 4.96	40.89	4.71

Ethyl esters of γ- or ε-bromo-δ-keto acids. A six- to sevenfold excess of absolute ethyl alcohol was added to the dibromides (I - V) in the cold and with stirring; the dibromides dissolved completely in the alcohol with considerable evolution of heat. After 30-60 minutes, the reaction mixture was poured into cold water,

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[*] Treatment of the dibromolactones (II) and (V) had to be carried out with very vigorous stirring while cooling to −30°; otherwise, the bromoketo acids (VI) and (IX) could not be isolated in the crystalline form owing to their further conversion.

TABLE 2

Compound	B.p., °C	n_D^{20}	d_4^{20}	MR_D		Yield, %	Found %		Calculated %	
				found	calc.		C	H	C	H
Ethyl ester of 5-oxo-4-bromo-4-methylhexanoic acid (X)	134–135 (12 mm)	1.4700	1.3090	53.51	53.37	65	43.24 43.31	6.27 6.15	43.04	6.02
Ethyl ester of 5-oxo-4-bromohexanoic acid (XI)	124–126 (10 mm)	1.4640	1.3352	49.00	49.46	72	40.62 40.90	5.71 5.78	40.53	5.52
Ethyl ester of 5-oxo-6-bromo-4,4-dimethylhexanoic acid (XII)	162–163 (10-12mm)	1.4749	1.2860	58.03	57.81	80	45.61 45.70	6.35 6.51	45.30	6.46
Ethyl ester of 5-oxo-6-bromo-4,4,6-trimethylheptanoic acid (XIII)	145–147 (8-10mm)	1.4742	1.2342	66.80	67.04	84	49.43 49.28	7.18 7.13	49.13	7.55
2-(β-carboxyethyl)-cyclopentene-2-one (XV)*	149–150 (10-12mm)	1.4780	1.0760	47.92	47.37	40	65.49 65.62	7.94 7.95	65.80	7.74

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* EM_D = 0.55.

and the aqueous alcohol solution was extracted with ether. The constants, yields, and analyses of these esters (X - XIII), determined after distillation of the esters under vacuum, are presented in Table 2.

Vacuum distillation of the bromo-substituted ester XIV, obtained from dibromolactone V, was accompanied by splitting out of hydrogen bromide, which led to the ethyl ester of unsaturated δ-keto acid XV.

Counter synthesis of the ethyl ester of 5-oxo-4-bromohexanoic acid (XI). 12 g (0.048 mole) of dioxane dibromide was added in small portions, while cooling with water, to 7 g (0.044 mole) of the ethyl ester of γ-acetylbutyric acid [3], and the mixture was allowed to stand for 0.5 hour. After distillation of the dioxane and vacuum distillation of the residue, there was obtained 5 g (50% yield) of ester XI, b.p. 123-124° at 10 mm, n_D^{20} 1.4650; d_4^{20} 1.3360.

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PREPARATION AND INVESTIGATION OF SOME PROPERTIES OF RUBIDIUM AND CESIUM GLASSES

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(Presented by Academician A. N. Terenin, November 28, 1958)

The study of complex silicate glasses in which the only alkali component is rubidium or cesium is of great interest, since it permits broadening of our ideas on the effect of the nature of the alkali ion on the properties of the glass, and, in particular, it permits a more complete study of the processes occurring during interaction of the glass with a solution. As is well known, this interaction leads to the origination of differences in potentials at the glass-solution boundary, which are the result of ion exchange between the glass and the solution. Therefore, the investigation of glasses containing rubidium and cesium ions is of great significance in connection with the theory of glass electrodes, broadening the possibility of obtaining glass electrodes which are reversible with respect to alkali ions.

However, the preparation of rubidium and cesium glasses meets with difficulties as to methods for such preparation, these difficulties being connected, first of all, with the infusibility of such systems. Therefore, only isolated cases of information are available in the literature regarding rubidium glasses, and, apparently, cesium glasses have not been generally described. Thus, Waterton and Turner [1] prepared a rubidium glass of the composition 75% SiO_2, 10% CaO, and 15% Rb_2O,* which was fused at a temperature of 1500°; a similar batch containing cesium oxide in place of rubidium oxide did not fuse even at a temperature of 1650°. Perley [2] attempted to prepare glasses with a large rubidium and cesium content in order to study their electrode properties; however, he was unsuccessful.

It should be noted that in pH-responsive electrode glasses there are sometimes used small additions of rubidium and cesium (2-3%), which obstruct the entry of sodium ions into the glass and thereby decrease the alkali error of the glass electrode [2].

Kracek [3], studying the locus of the liquidus of cristobalite, also prepared glasses with small contents of rubidium and cesium oxides 3.50-2.59% Rb_2O, 2.34-3.35% Cs_2O).

Since we undertook the preparation of rubidium and cesium glasses in connection with a study of the properties of the glass electrode, we first of all attempted to synthesize a glass of the composition 71% SiO_2, 11% B_2O_3, 3% Al_2O_3, and 15% Rb_2O, similar to sodium and potassium glasses which exhibit the respective metal electrode functions. However, this glass was very infusible – the batch did not melt even at a temperature of 1500°. In order to reduce the melting point and viscosity of the glass, the aluminum oxide and part of the silica were replaced by boric oxide. A small amount (5%) of calcium oxide was added to increase the chemical stability of the glass. Two rubidium glasses containing 20-30% B_2O_3 (Glasses No. 5 and 6 in Table 1) were fused. But this glass was still very viscous. Part of the calcium oxide was replaced with magnesium oxide to reduce the viscosity. As a result, rubidium and cesium glasses of two compositions were synthesized: 60% SiO_2, 20% B_2O_3, 15% R_2O, 2% MgO, and 3% CaO and 50% SiO_2, 30% B_2O_3, 15% R_2O, 2% MgO, and 3% CaO, where R_2O = Rb_2O and Cs_2O (Glasses Nos. 8, 9, 10, and 11).

It should be pointed out that there is a possibility of preparing a glass of intermediate composition, for example, one containing 25% B_2O_3. Attempts were also made to prepare a rubidium glass with a lower boric

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*Here and in the remainder of this communication, all glass compositions are given in mole per cent.

TABLE 1

Compositions of the Glasses Synthesized*

Glass No.	mole % SiO₂	B₂O₃	Na₂O	K₂O	Rb₂O	Cs₂O	MgO	CaO	wt. % SiO₂	B₂O₃	Na₂O	K₂O	Rb₂O	Cs₂O	MgO	CaO
1	60	20	15				2	3	58.36	22.55	15.05				1.31	2.72
2	50	30	15				2	3	47.90	33.31	14.83				1.28	2.68
3	60	20		15			2	3	54.13	20.92		21.21			1.21	2.53
4	50	30		15			2	3	44.47	30.93		20.92			1.19	2.49
5	60	20			15			5	44.59	17.23			34.70			3.47
6	50	30			15			5	36.73	25.55			34.29			3.43
7	65	15			15		2	3	48.79	13.05			35.05		1.01	2.10
8	60	20			15		2	3	44.77	17.30			34.84		1.00	2.09
9	50	30			15		2	3	36.87	25.63			34.43		0.99	2.07
10	60	20				15	2	3	38.05	14.71				44.60	0.85	1.78
11	50	30				15	2	3	31.38	21.83				44.17	0.84	1.76
12	40	40				15	2	3	24.86	28.82				43.74	0.83	1.74

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* Compositions based on synthesis data.

oxide content (No. 7) and a cesium glass with a higher boric oxide content (No. 12). However, these glasses crystallized readily. For comparison, sodium and potassium glasses of the same composition (Nos. 1,2,3, and 4) were prepared. Thus, the glasses synthesized constitute two series containing 20 (Series I) and 30% (Series II) boric oxide.

The metal carbonates, boric acid, and silicon dioxide were used in the preparation of the glasses. The sodium, potassium, and rubidium glasses were fused in small platinum crucibles in a furnace with four Silit resistors at a temperature of 1200-1450°; the cesium glasses were fused in corundum crucibles in a Kryptol furnace at a temperature of 1600°. These rubidium and cesium glasses possessed high refraction ("crystal luster").

The glasses of both series were subjected to preliminary investigation.

In order to compare the characteristics of these glasses, tests of their chemical stability with respect to water were carried out by the method of Kohlrausch [4], which requires a small amount of the glass. This method is based on measurement of the electrical conductivity of the water after agitation of glass powder in it. The glass was powdered in an agate mortar. The fraction passing through a 200 mesh sieve was selected, and the powder was then freed from fines by washing with ether. The experimental results are presented in Table 2. For comparison, the chemical stability of 3 electrode glasses which were metal-responsive in a wide pH interval was also determined.

Values of the specific conductivity are given in the table with a correction for the original conductivity of the water, and values are also given for the magnitude of Δ, which characterizes the depth of the disintegration of the glass [5,6]:

$$\Delta = \frac{\delta F d}{v} = \frac{\varkappa - \varkappa_0}{\frac{p}{100 A} \lambda^{18}_{ROH}}\,.$$

where δ is the thickness of the disintegrated layer, F is the total surface of the glass, d is the density of the glass, v is the volume of water, $\varkappa - \varkappa_0$ is the specific conductivity of the alkali passing into solution, p is the percentage content of R_2O, A is the equivalent weight of R_2O, λ^{18}_{ROH} is the equivalent conductivity of the alkali at infinite dilution and 18°. If it is assumed that v, F, and d for all of the glasses investigated remain constant, then the magnitude of Δ will be proportional to the thickness of the disintegrated layer. For glasses available in large amounts, the chemical stability was determined by the acceleration method developed by the All-Union Institute for Glass [7]. The results of these experiments, expressed in mg of R_2O, are presented in Table 2,

TABLE 2

Chemical Stability of the Glasses at 18°

Glass composition, mol. %	Agitation time, hours	Na_2O $(n - n_1)\cdot 10^{4}$	Na_2O $\Delta\cdot 10^{4}$	Na_2O, mg	K_2O $(n - n_1)\cdot 10^{4}$	K_2O $\Delta\cdot 10^{4}$	K_2O, mg	Rb_2O $(n - n_1)\cdot 10^{4}$	Rb_2O $\Delta\cdot 10^{4}$	Cs_2O $(n - n_1)\cdot 10^{4}$	Cs_2O $\Delta\cdot 10^{4}$
60% SiO_2 20% B_2O_3 15% R_2O 2% MgO 3% CaO	1	21.0	20.6		25.2	24.4	0.38	33.3	37.2	20.0	28.4
	2	28.0	28.3		30.6	28.4		44.5	49.5	20.0	30.0
50% SiO_2 30% B_2O_3 15% R_2O 2% MgO 3% CaO	1	85.7	82.3		82.7	78.0		80.0	60.5	12.0	17.8
	2	130.0	125.0		123.5	122.0		100.0	120.0	15.0	23.0
71% SiO_2 11% B_2O_3 3% Al_2O_3 15% R_2O	1	16.0	16.2	0.22	17.1	18.2	0.19				
	2	18.3	17.6		20.4	19.2					
69% SiO_2 6% B_2O_3 5% Al_2O_3 20% R_2O	1			0.30*	27.1	27.3	0.54				
	2				40.7	30.0					
61% SiO_2 9% B_2O_3 5% Al_2O_3 25% R_2O	1			1.55*	145.0	98.5	7.03				
	2				167.0	100.0					

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*Data taken from the work of M. M. Shults and L. G. Aio.

Comparing the values characterizing chemical stability, it can be noted that, for glasses with a high boric oxide content, the sodium and potassium glasses have approximately the same stability, while for electrodes of aluminoborosilicate glasses, the stability of the sodium glasses is higher than that of the potassium glasses. The rubidium glass of Series I is less stable, and that of Series II is more stable, than sodium and potassium glass. The cesium glasses, particularly of Series II, are considerably more stable than glasses of similar composition containing other alkali ions. It is possible that the increased stability of the cesium glasses is connected with the transfer of a small amount of alumina from the corundum crucibles to the glass. The alumina impurity in these glasses was detected by spectroscopic analysis.

As to the electrode characteristics of these glasses, we carried out preliminary potential measurements in sodium chloride solutions with electrodes of glass No. 1, and we also measured the resistance of electrodes of glass No. 3, which was very high (10^5 MΩ). The potential was clearly dependent on the concentration of sodium ions, but the sodium response was only 80-90% of theoretical.

As a clarification of the nature of the reaction of these glasses with solutions, it was also of interest to investigate the absorption of cations by these glasses. Such a study can give some information as to the nature of the bonds of the alkali ions in the glass. In this connection, the sorption of rubidium ions on glasses of Series II (Nos. 2, 4, and 9) in 0.01 N RbCl was studied by means of tagged atoms. The Rb^{86} isotope (T = 19.5 days) was used as the radioactive indicator. The experimental results, expressed as the number of rubidium atoms absorbed over a specific time interval by glass plates (working surface approximately 1.5 sq. cm.), are presented in Figure 1. For comparison, on this same graph is shown the sorption of rubidium on a potassium electrode glass (61% SiO_2, 9% B_2O_3, 5% Al_2O_3, and 25% K_2O).

The results obtained are qualitative, since the error in measurement with the method used for the preparation of the glass plates was 25%. Therefore, they permit judgement only of the overall nature of the process.

As seen from Figure 1, the absorption of rubidium on sodium and potassium glasses was approximately the same and was somewhat greater than on rubidium glass, which, apparently, is a consequence of the difference in surface properties and internal structure of these glasses.

Thus, as a result of the work carried out, ratios of components were found which permit preparation of glasses with a large content of rubidium and cesium oxides. This was successful owing to the introduction into the glass composition of a large amount of boric oxide in mixtures of magnesium and cesium oxides. On the basis of this first experiment, routes can be planned for the preparation of rubidium and cesium glasses with metal electrode functions.

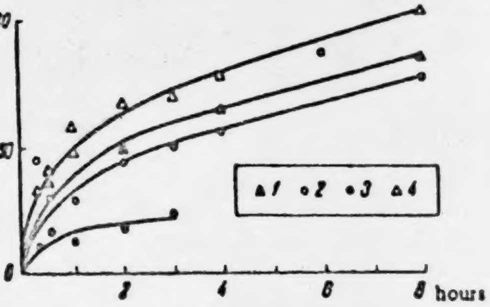

Fig. 1. Sorption of rubidium ions on different glasses: 1) sodium, 2) potassium, 3) rubidium, 4) potassium electrode.

In conclusion, the authors express their deep appreciation to Prof. B. P. Nikolsky for constant attention and interest in the work, and also to Academician of the Academy of Sciences USSR M. A. Bezborodov and Prof. A. I. Avgustinik for valuable advice.

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HOMOLYTIC ISOMERIZATION OF 1,1,1-TRICHLORO-2-BROMOPROPENE

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Until recently, the question of the possibility of free radical rearrangement in solution was debatable (cf., for example, [1-3]). Up to the present, rearrangements in radicals by phenyl group migration has been described [4-10].

In our work by two of the authors of the present article and L. I. Zakharkin [11], rearrangement was found to occur in a radical of the structure $CCl_3\dot{C}HCH_2X$ by migration of chlorine according to:

$$CCl_3\dot{C}HCH_2X \rightarrow \dot{C}Cl_2CHClCH_2X, \text{where } X = Br, CCl_3 \qquad (1)$$

This rearrangement occurs during homolytic addition of hydrogen bromide or bromotrichloromethane to 1,1,1-trichloropropene.

In the present article, we report on the homolytic isomerization of 1,1,1-trichloro-2-bromopropene to 1,1,2-trichloro-3-bromo-1-propene according to the scheme:

$$CCl_3CBr = CH_2 \rightarrow CCl_2 = CCl - CH_2Br \qquad (2)$$

1,1,1-trichloro-2-bromopropene has the following constants: b.p. 57-58°/15 mm, n_D^{20} 1.5323, d_4^{20} 1.8493.

On standing, after a certain induction period (1-2 days), or on irradiation with a mercury lamp for several minutes without heating this compound isomerized completely to 1,1,2-trichloro-3-bromo-1-propene with a b.p. of 78-79°/19 mm, n_D^{20} 1.5550, d_4^{20} 1.8335. This isomerization was conveniently traced by measuring the index of refraction. The addition of hydroquinone or dimethylaniline to the 1,1,1-trichloro-2-bromopropene prevented the isomerization, and samples containing inhibitor were stored for many months without change.

We assume that the isomerization proceeds according to the following scheme:

$$\begin{aligned}
&a)\ C_3H_2Cl_3Br \rightarrow \dot{Br} + C_3H_2\dot{Cl}_3\\
&b)\ CCl_3CBr = CH_2 + \dot{Br} \rightarrow CCl_3\dot{C}BrCH_2Br\\
&c)\ CCl_3\dot{C}Br - CH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CClBrCH_2Br\\
&d)\ \dot{C}Cl_2CClBrCH_2Br + CCl_3CBr = CH_2 \rightarrow CCl_2 = CClCH_2Br + C\dot{C}l_3CBrCH_2Br
\end{aligned} \qquad (3)$$

Thus, here, apparently, rearrangement occurs in the radical in a manner completely similar to the rearrangement previously mentioned [compare Schemes (1) and 3 (c)].

Our case of homolytic isomerization of $CCl_3CBr = CH_2$ is interesting in that this isomerization differs in its course from anionotropic allylic rearrangement of this same compound. We showed that 1,1,1-trichloro-2-bromopropene undergoes allylic rearrangement under the influence of antimony pentachloride or aluminum chloride with the formation, in 90% yield, of 1,1,3-trichloro-2-bromo-1-propene, b.p. 81-82°/21 mm, n_D^{20} 1.5522, d_4^{20} 1.8954. These rearrangements are compared in the scheme:

$$CCl_3-CBr=CH_2\rightarrow\left\{\begin{array}{l}\xrightarrow{h\nu}CCl_2=CCl-CH_2Br\\ \xrightarrow[SbCl_5]{}CCl_2=CBr-CH_2Cl\end{array}\right.\qquad(4)$$

The methods of preparation of the substances investigated and proof of their structure were, briefly, the following.

The initial material for the preparation of 1,1,1-trichloro-2-bromopropene was 1,1,1-trichloro-2,3-dibromopropane, which was obtained by the action of bromine, without irradiation, on 1,1,1-trichloropropene in acetic acid medium with a yield of 80% of theoretical.

1,1,1-Trichloro-2-bromopropene was obtained as the sole product of the action of potassium hydroxide on 1,1,1-trichloro-2,3-dibromopropane, with cooling (yield, 71% of theoretical):

$$\underset{(I)}{CCl_3CHBrCH_2Br}\xrightarrow{KOH}\underset{(II)}{CCl_3CBr=CH_2}\qquad(5)$$

The allylic isomer of this compound – 1,1,3-trichloro-2-bromo-1-propene – was prepared according to the scheme:

$$CCl_2=CHCH_2Cl+Br_2\rightarrow\underset{(III)}{CCl_2BrCHBrCH_2Cl}\xrightarrow{KOH}\underset{(IV)}{CCl_2=CBrCH_2Cl}\qquad(6)$$

The structure of substance III was confirmed by hydrolysis with nitric acid (sp. gr. 1.52) with the formation of α-bromo-β-chloropropionic acid in good yield; the latter, by the action of alcoholic alkali, gave α-bromoacrylic acid.

The isomerization of substance II to substance IV by the action of $SbCl_5$ [Scheme (4)] confirms the structure of II, since the reverse isomerization of substances of Type IV to substances of Type II is unknown.

1,1,2-trichloro-3-bromo-3-propene, the product of the homolytic isomerization of substance II [Scheme (2)], was synthesized by a known route according to:

$$CCl_2=CClCH_2Cl\xrightarrow[(CH_3)_2CO]{NaBr}\underset{(V)}{CCl_2=CClCH_2Br}\qquad(7)$$

All three trichlorobromopropenes, II, IV, and V, which were prepared both by isomerization according to Scheme (4) and by an independent route according to Schemes (6) and (7), were identified in the form of the hydrochlorides of their diethylamino derivatives, prepared according to Schemes (8) and (9) in yields above 60% of theoretical.

$$\begin{array}{l}\underset{(II)}{CCl_3CBr=CH_2}+(C_2H_5)_2NH\rightarrow\underset{(VI)}{CCl_2=CBrCH_2N(C_2H_5)_2\cdot HCl}\\ \qquad\underset{(IV)}{CCl_2=CBrCH_2Cl}+(C_2H_5)_2NH\longrightarrow\end{array}\qquad(8)$$

$$\begin{array}{l}\underset{(V)}{CCl_2=CCl-CH_2Br}+2\,(C_2H_5)_2NH\rightarrow CCl_2=CClCH_2N(C_2H_5)_2\rightarrow\\ \qquad\xrightarrow{HCl}\underset{(VII)}{CCl_2=CClCH_2N(C_2H_5)_2\cdot HCl}\end{array}\qquad(9)$$

hydrochloride (VII) did not depress the melting point when mixed with a known sample previously prepared [12].

Of the other observations made in the course of this work, the following should be mentioned.

By the action of a solution of potassium hydroxide in ethyl cellosolve on 1,1,3-trichloro-1,2-dibromopropane, with cooling, after the usual treatment there was obtained a mixture of products from which, by vacuum distillation in a column, was isolated the previously mentioned [Scheme (5)] 1,1,3-trichloro-2-bromo-1-propene (IV) with a b.p. of 81-82°/21 mm, n_D^{20} 1.5522, d_4^{20} 1.8955, which was identical in all properties to the substance obtained by allylic isomerization of 1,1,1-trichloro-2-bromopropene; a mixture of dibromides of the composition $C_3H_2Cl_2Br_2$ was also obtained. By reaction with diethylamine in methyl alcohol medium, this dibromide gave a diethylamino derivative which was identical with the previously described 1,1-dichloro-2-bromo-3-diethylamino-1-propene. The preparation of the indicated diethylamino derivative shows that the dibromide must have the structure $CCl_2Br-CBr=CH_2$ or $CCl_2=CBrCH_2Br$.

1,1,1-Trichloro-2-bromopropene (II) and its allylic isomer IV, prepared both by isomerization and according to Scheme (6), when reacted with benzene in the presence of $AlCl_3$ gave, in good yield, the same compound of the structure $C_6H_5CH_2CBr=CCl_2$.

It should also be noted that a reaction carried out between 1,1,1-trichloropropene and bromine in chloroform medium with irradiation by an incandescent lamp (150 watts) gave 1,1,1-trichloro-2,3-dibromopropane contaminated with an isomeric dibromotrichloropropane (cf. [13]).

TABLE 1

Formula	B. p. deg/mm	n_D^{20}	d_4^{20}	MR		C, %		H, %	
				found	calc.	found	calc.	found	calc.
$CCl_3CHBrCH_2Br$	69/2	1.5590	2.1751	48.58	48.19				
$CCl_2BrCHBrCH_2Cl$	68–69/1	1.5678	2.1874	48.64	48.18	11.60 11.71	11.80	0.98 0.98	0.99
$CCl_3CBr=CH_2$	87–88/15	1.5723	1.8493	37.82	37.95				
$CCl_2=CBr-CH_2Cl$	81–82/21	1.5522	1.8955	37.83	37.95	15.83 16.00	16.08	0.83 0.77	0.89
$CCl_2=CClCH_2Br$	78–79/19	1.5500	1.8935	38.23	37.95	15.80 15.72	16.08	0.85 0.87	0.82
$CCl_2=CBrCH_2N(C_2H_5)_2$*	90/1	1.5079	1.4060	55.23	55.50	32.35 32.39	32.21	4.73 4.81	4.63
$CCl_2=CBrCH_2N(C_2H_5)_2\cdot HCl$**						28.14 28.58	28.20	4.65 4.45	4.60
$C_6H_5CH_2CBr=CCl_2$	97–98/2	1.5840	1.5666	57.19	57.19	40.60 40.80	40.64	2.56 2.64	2.65
$C_3H_2Cl_2Br_2$***	97–98/21	1.5645	2.1957	41.00	40.85	13.38 13.40	13.40	0.73 0.75	0.75

---

* Found %: N 5.43, 5.26. Calculated %: N 5.36.

** M. p. 144-145°.

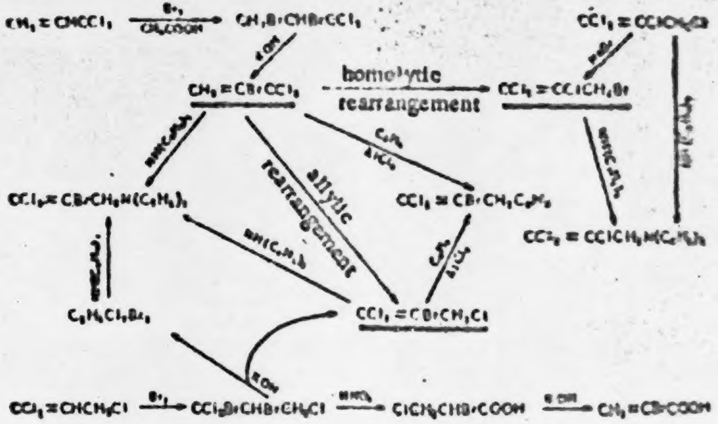
*** Prepared by the action of potassium hydroxide on $CCl_2BrCHBrCH_2Cl$.

The latter compound could not be isolated in a pure form. Judging from the fact that on heating this mixture with nitric acid (sp. gr. 1.52) α-chloro-β-bromopropionic acid was isolated in approximately 20% yield, it can be assumed that the mixture contained, as an impurity, 1,1,2-trichloro-1,3-dibromopropane (pure 1,1,1-trichloro-2,3-dibromopropane, on heating with nitric acid—sp. gr. 1.52—gives only neutral products containing nitrogen). This conclusion is in agreement with the fact that the action of potassium hydroxide on the mixture of dibromotrichloropropanes gave a mixture of bromotrichloropropenes which could be separated in the form of diethylamino derivatives of the structure.

$$CCl_2=CBrCH_2N(C_2H_5)_2 \text{ и } CCl_2=CClCH_2N(C_2H_5)_2$$

The formation of 1,1,2-trichloro-1,3-dibromopropane can be explained on the basis that, under the described conditions, in contrast to reaction in acetic acid medium without irradiation, there is also bromination by a homolytic mechanism accompanied by rearrangement in the radical according to the scheme:

$$
\begin{gathered}
\mathrm{CCl_3-CH=CH_2 + Br \rightarrow CCl_3\dot{C}HCH_2Br \xrightarrow{rearrangement} \dot{C}Cl_2CHClCH_2Br} \\
\mathrm{\dot{C}Cl_2CHClCH_2Br + Br_2 \rightarrow BrCCl_2CHClCH_2Br + \dot{B}r}
\end{gathered} \qquad (10)
$$


CH2=CHCCl3
Br2
CH3COOH
CH2BrCHBrCCl3
KOH
CH2=CBrCCl3
homolytic
rearrangement
CCl2=CClCH2Br
CCl2=CClCH2Cl
KOH
CCl2=CBrCH2N(C2H5)2
NH(C2H5)2
allylic
rearrangement
C6H6
AlCl3
CCl2=CBrCH2C6H5
NH(C2H5)2
CCl2=CClCH2N(C2H5)2
C6H6Cl2Br2
CCl2=CBrCH2Cl
C6H6
AlCl3
KOH
CCl2=CHCH2Cl
Br2
CCl2BrCHBrCH2Cl
HNO3
ClCH2CHBrCOOH
KOH
CH2=CBrCOOH

The reactions carried out in the present work are represented in the above scheme.* Some of the constants and analyses of the compounds prepared are given in Table 1.

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SYNTHESIS OF NITRILES FROM ALCOHOLS AND AMMONIA OVER OXIDE CATALYSTS

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(Presented by Academician A. V. Topchiev, October 12, 1956)

In recent years, more and more of the materials previously difficult to obtain have become products of tonnage production. This is completely true of nitriles. Such nitriles as acrylonitrile and adiponitrile have found broad industrial application. Acetonitrile and nitriles of other fatty acids have found even greater use. The production of nitriles by direct reaction of ammonia with organic compounds has attracted the attention of numerous investigators, both here and abroad. This interest has been caused by attempts to find methods for the production of acetonitrile and other nitriles in large amounts from relatively cheap raw material. Such cheap raw materials are the gaseous hydrocarbons from thermal and catalytic cracking of petroleum as well as low molecular weight paraffinic hydrocarbons. For some time past, the production of nitriles from olefins and ammonia has received rather widespread attention in the literature; several articles have also been devoted to the reaction of ammonia and paraffinic hydrocarbons. The reaction of alcohols with ammonia has been considered in many papers, although chiefly from the point of view of the production of amines.

TABLE 1

Physicochemical Properties of Acetonitrile

CH_3CN	B. p., °C, and press., mm Hg	n_D^{20}	d_4^{20}	Mol. wt.	MR	M. p. of acetyl-phloro-glucinol °C	Elemental composition, %	
							H	C
Synthesized	80.0—81.5/730	1.3432	0.7819	42	11.04*	216—218	58.73	7.45
Lit. data [8] and Theoret.	81.6/760	1.3442	0.7828	41.1	11.13	218.5 (⁹)	58.52	7.36

Several patents also report the production of nitriles from alcohols and ammonia. Thus, a British patent [1] described the production of butyronitrile in 45% yield from butyl alcohol and ammonia in the vapor phase over reduced nickel catalyst at 150° and a 2- to 5.5-fold excess of ammonia. Other investigators have also established the formation of nitriles as intermediate products during the production of amines [2]. n-Butyronitrile and benzonitrile were obtained by Denton and Bishop from n-butyl alcohol and benzyl alcohol, respectively, in the presence of molybdena-alumina catalyst with a twofold excess of ammonia at a temperature of 435° [3]. A British patent [4] describes the production of nitriles from primary alcohols and ammonia in the vapor phase in the presence of catalysts containing oxides of molybdenum, tungsten, and vanadium and salts of molybdenum and nickel. A Danish patent indicates the possibility of producing nitriles from the corresponding alcohols and ammonia over a Zn catalyst at 350-475°. Thus, the nitrile $C_6H_{13}CN$ was obtained from n-heptyl alcohol in 60% yield at 440°. Ethyl alcohol and ammonia give acetonitrile in 40% yield over reduced copper at 301-344° [6,7].

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* MR, calculated theoretically from atomic refractions, is 11.25.

We investigated the reaction of ethyl and isoamyl alcohols with ammonia in the presence of molybdena-alumina catalyst (10% MoO_3, 90% Al_2O_3).

The alcohol was fed at a space rate of 0.13 liter/liter of catalyst per hour, regulated by a clockwork mechanism, to the catlyst-filled reactor, which was installed in a catalyst furnace with a temperature regulator. After drying with solid potassium hydroxide, the ammonia was fed from a cylinder at the required rate regulated by a galvanometer. The reaction products were condensed first in a receiver fitted with a reflux condenser, and then in traps cooled with dry ice in isopropyl alcohol. The effluent gases, freed from ammonia by passage through water and through a tube of solid ammonium thiocyanate, were measured with a gas meter and collected in a gasometer for analysis. Analysis of the gas was carried out in a VTI apparatus.

The experiments were carried out over three-hour periods. The catalyst was regenerated with air until the coke, formed during the reaction, was completely burned off. The catalyzates, after elimination of the ammonia and ammonium cyanide by boiling on a water bath with a reflux condenser, were distilled from a Favorsky flask. A broad fraction, boiling to 90°, was removed; the residue was water. This fraction was then redistilled, and a fraction boiling at 74-77°, acetonitrile-water azeotrope, was collected. Anhydrous acetonitrile was obtained by drying the azeotrope over solid potassium hydroxide and subsequent distillation over P_2O_5. The acetonitrile was identified by a series of qualitative tests, the physicochemical constants, and the preparation of the condensation product with phloroglucinol (Table 1).

The effect of temperature on the yield of acetonitrile was studied in the experiments with ethyl alcohol.

TABLE 2

Yields and Physicochemical Properties of the 70-128° Fraction (alcohol space rate = 0,13 hour^{-1}; i-$C_5H_{11}OH$: NH_3 = 1 : 3).

Temperature, °C	Yield of 70-128° fraction, wt. % of alcohol	Mol. wt.	d_4^{20}	n_D^{20}
319	33	83	0.7900	1.3981
356	27	81	0.7972	1.3959
418	21	74	0.7924	1.3949
458	21	71	0.7932	1.3918
487	27	59	0.7944	1.3783
510	23	60	0.7927	1.3741

We present below the data obtained, from which it is seen that the formation of acetonitrile began at a temperature above 350°, and, with a further increase in temperature, the yield increased to a definite maximum, after which it began to fall owing to an increase in side reactions, the decomposition of ammonia and of the acetonitrile formed (space rate of the alcohol 0.13 hours^{-1}; C_2H_5OH : NH_3 = 1 : 2):

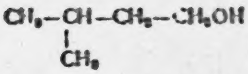
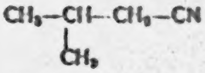
Temperature, °C	350	415	468	487	510	538
Yield of acetonitrile, mol. %: on NH_3:	–	6,6	7,8	12,6	10,4	4,2
on $C_2H_5H_5OH$	–	12,2	14,4	22,9	19,5	11,8
Yield of NH_4CN, mol. % of alcohol charged	–	1,2	2,5	2,7	4,8	10,2

Traces of pyridine were observed during the work with ethyl alcohol at temperatures below 400°. All fractions had an increased index of refraction and the characteristic odor of pyridine. The presence of pyridine was established by the qualitative reaction with nickel thiocyanate and copper sulfate [10]. Moreover, the small upper layer had an index of refraction of 1,5057, close to that given in the literature for pure pyridine (1,5092).

The reaction of isoamyl alcohol with ammonia was also studied. After removal of the ammonia and ammonium cyanide, which were formed in small amounts, the catalyzate separated into two layers. Acetonitrile was not detected in the aqueous layer by qualitative reaction with $FeCl_3$. The upper layer, after drying with solid KOH, was distilled from a Favorsky flask, and a fraction boiling at 28-70° (n_D^{20} = 1,3778) and a broad

TABLE 4

Preparation of Nitriles from n-Pentane and Ethyl and Isoamyl Alcohols

Starting material	Optimum temperature, °C	Mol. ratio of starting material to NH$_3$	Nitrile	Nitrile yield based on material processed, wt.%
 $CH_3-CH(CH_3)-CH_2-CH_2OH$	319	1 : 3	 $CH_3-CH(CH_3)-CH_2-CN$	18
$CH_3-(CH_2)_3-CH_3$	510	1 : 2	CH_3CN	28
C_2H_5OH	487	1 : 1.87	CH_3CN	20.4

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CHEMICAL STRUCTURE AND THE PHYSICOCHEMICAL PROPERTIES OF HYDROCARBONS*

NEW RULES AND METHODS OF CALCULATION

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(Presented by Academician A. A. Balandin, November 17, 1956)

In previous papers [1-5], we showed that a number of physicochemical properties of paraffinic hydrocarbons (alkanes), C_nH_{2n+2} – molar volume, molar refraction, heat of formation, heat of combustion, heat of vaporization, etc. – can be described by the equation **

$$P = \sum_{i \leqslant j = 1}^{4} n_{ij} P_{ij}, \tag{1}$$

where P is the physicochemical property per mole of substance (or its average value per molecule), n_{ij} is the number of $C_i - C_j$ bonds in the molecule, P_{ij} is the value of the given physicochemical property $N_A\, C_i - C_j$ bonds (or for one $C_i - C_j$), i, j are indices denoting whether the carbon atoms in the $C_i - C_j$ bond are primary, secondary, tertiary, or quaternary. It was also shown [3] that Equation (1) can be put into the form

$$P = 2P_{12} + (n-3)P_{22} + \sum_{i,j<1}^{4} n_{ij} G_{ij}\,. \tag{2}$$

where, $G_{12} = G_{22} = 0$, and the remaining values of G_{ij} are related to P_{ij} by the equations

$$G_{13} = P_{13} - \frac{2}{3}P_{12} - \frac{1}{3}P_{22}; \quad G_{24} = P_{24} + \frac{1}{2}P_{12} - \frac{3}{2}P_{22}$$
$$G_{14} = P_{14} - \frac{1}{2}P_{12} - \frac{1}{2}P_{22}; \quad G_{33} = P_{33} + \frac{2}{3}P_{12} - \frac{5}{3}P_{22}$$
$$G_{23} = P_{23} + \frac{1}{3}P_{12} - \frac{4}{3}P_{22}; \quad G_{34} = P_{34} + \frac{5}{6}P_{12} - \frac{11}{6}P_{22}$$
$$G_{44} = P_{44} - P_{12} - 2P_{22}$$

Equations (1) and (2) hold for any branched or normal alkanes. In particular, for normal alkanes we have from (1) or (2):

$$P_{\text{norm}} = 2P_{12} - 3P_{22} + nP_{22} \tag{3}$$

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*This paper contains part of the results presented by the author at the symposia held at Moscow State University in April, 1956.

**The notation of this article differs slightly from that of the preceding papers; the correspondence is easily established by comparison.

It has been shown [3] that all alkanes can be divided into groups such that, independently of the number of carbons in the alkanes falling into a given group, for the alkanes of the given (for example, the m-th) group the following condition will hold approximately:

$$\Delta^{(m)} = \sum_{i<j-1}^{4} n_{ij}^{(m)} G_{ij} \approx \text{const}. \tag{4}$$

From (2) and (4) it follows that for alkanes of the m-th group

$$P_n^{(m)} = 2P_{12} - 3P_{22} + \Delta^{(m)} + nP_{22}. \tag{5}$$

where n is the number of C atoms in the alkane, and the remaining values on the right side of the equation are constants. Consequently, in each group of alkanes, the physicochemical property, P, being considered is linearly dependent on the number of carbon atoms in the alkanes of the group. Therefore, the members of each group display homologous properties in a similar manner to the members of the series of normal alkanes. From (5), it also follows that the straight lines described by Equation (5) must be parallel for the different groups and differ only by a constant displacement along the P axis. Analysis of considerable data on molar volume, heat of formation, refraction, heat of vaporization, and vapor pressure shows that the values predicted from theory are very well confirmed by the experimental data for these physicochemical properties of the alkanes.

It is evident that the rule reflected by Equation (5) can be successfully used for the calculation of a series of physicochemical properties of the higher alkanes from the physicochemical properties of the lower alkanes. Actually, if values of P are known for two alkanes of the m-th group, the coefficients of Equation (5) are determined, and values of P for all the other alkanes of the same group (with other values of n) can be calculated from Equation (5).

Since values of P_{12} and P_{22} can be determined from values of the appropriate physicochemical properties of the normal alkanes, and $\Delta^{(m)}$ can be determined from the value of this same physicochemical property of a single alkane of the m-th group, data on the physicochemical properties of the normal alkanes can be used for the calculation of a given physicochemical property for all alkanes, and experimental value for the property P is required for only one of the alkanes of the same group. It is evident that the possibility, offered by Equation (5), for calculating the physicochemical properties of the higher alkanes considerably extends and supplements earlier known methods of calculation.

As was shown earlier [3], for all classes of hydrocarbons containing alkyl radicals, the equation for calculating a physicochemical property P can be put into the form:

$$P = C + \sum_{i,<j-1}^{4} n_{ij} P_{ij}. \tag{6}$$

where C is a constant for a given structural nucleus (naphthenic rings, benzene ring, a nucleus with double bonds, etc.) to which are added the alkyl groups, and also characteristic of the substitution of the nucleus (number and order of substituting alkyl radicals on the nucleus), and $\Sigma n_{ij} P_{ij}$ refers to the substituting alkyl radicals. It is easily seen that hydrocarbons with a given nucleus (C = const) can be divided into groups according to the nature of the substituting alkyl radicals such that for each group (for example, the m-th), Equation (6) can be transformed into the form:

$$P_n^{(m)} = C^{(m)} + \Sigma n_{ij}^{(m)} G_{ij} + nP_{22}. \tag{7}$$

whence, for a given group:

$$C^{(m)} \sim \text{const}$$
$$\Sigma n_{ij}^{(m)} G_{ij} = \Delta^{(m)} \simeq \text{const}. \tag{8}$$

Then, Equation (6) reduces to the form:

$$P_n^{(m)} = C^{(m)} + \Delta^{(m)} + nP_{22}, \tag{9}$$

where all values except n are constant for a given group, and everything indicated above with respect to alkanes will hold with respect to hydrocarbons of other classes which contain alkyl radicals.

Analysis of the available data on molar volume, heat of formation, refraction, and certain other properties of hydrocarbons of various classes shows that the experimental data for hydrocarbons of the various classes confirm the predictions from theory if we consider the values on the basis of those groups of hydrocarbons into which they can be divided on the basis of Equation (9) and the previously presented Equation (3) for their series of physicochemical properties.

For such physicochemical properties as density and boiling point [which do not obey Equations (1 - 9)], (5) and (9) can be used as follows. For density we have:

$$d = \frac{M}{V},$$

where M is molecular weight and V is molar volume. Since for hydrocarbons of a given m-th group, both M and V follow a linear equation of the type of (5) or (9)

$$M^{(m)} = a^{(m)} + b \cdot n$$
$$V^{(m)} = g^{(m)} + h \cdot n,$$

where n is the number of C atoms in a hydrocarbon of the m-th group; the density of hydrocarbons of the m-th group is expressed by a fractional linear function of n.

$$d_n^{(m)} = \frac{a^{(m)} + b \cdot n}{g^{(m)} + h \cdot n}.$$

Based on an analysis of the dependence of heats of formation and vapor pressures on temperature for hydrocarbons of the m-th group, it can be shown that the boiling points, at a given pressure, of hydrocarbons of the m-th group can also be expressed, to a first approximation, by a fractional linear function of n.

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SULFOXIDATION OF METHANE WITH GASEOUS SULFUR DIOXIDE AND OXYGEN

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There has been practically no description of the sulfoxidation of methane in the literature, there being only individual indications of the conversion of methane under the action of certain sulfurizing agents. Methane has been slowly dissolved in fuming sulfuric acid [1]; however, the compounds resulting from this treatment were not isolated. Methane reacts thermally and thermocatalytically with sulfur trioxide with the formation of sulfur-containing derivatives and oxidation products [2,3].

Methanesulfonic acid and its derivatives are usually prepared by other methods. Alkali salts of methanesulfonic acid can be prepared from salts of sulfurous acid and methyl iodide [4] or from methyl iodide and diethylsulfite in the presence of potassium hydroxide [5]. Heating dimethylsufate with alkali metal sulfites [6] gives the corresponding salts of methanesulfonic acid and methylsulfuric acid, which are difficultly separable from each other.

Indirect methods for the preparation of methanesulfonic acid [7,8] are also described; however, there is no mention in the literature of the possibility of direct sulfoxidation of methane with gaseous sulfur dioxide and oxygen for the preparation of methanesulfonic acid. The present work, which we carried out using as reaction initiators various additives, ultraviolet light, x-ray irradiation, and high-frequency electrical discharge, had for its aim the investigation of the possibility of sulfoxidizing methane.

As a result of experiments carried out in quartz apparatus in static and flow systems, it was established that there is practically no sulfoxidation of methane by gaseous sulfur dioxide and oxygen under the influence of ultraviolet light. Only photochemical processes involving the oxidation of methane and of sulfur dioxide occurred under these conditions. Methane also did not undergo photochemical sulfoxidation in the presence of metallic mercury, acetic anhydride, palladium black, or benzoyl peroxide at low temperatures, but at elevated temperatures (200-400°C) methanesulfonic acid was formed with a yield of about 0.02 % of theoretical. In this case, the main processes were the oxidation of methane and of sulfur dioxide. The yield of sulfuric acid was 30-40 times that of methanesulfonic acid. Under the influence of x-rays, the initial gaseous materials reacted with the formation of only carbon monoxide and dioxide, hydrogen, water, and sulfur trioxide in amounts of the order of 2-5% of each. We were unable to detect the formation of methanesulfonic acid under these conditions.

The inertness of methane in the sulfoxidation reaction can be explained by the lack of appreciable dissociation of methane molecules with the formation of methyl radicals under the influence of ultraviolet light with a wavelength greater than 3000 A, and that the dissociation of methane molecules proceeds to some extent only at elevated temperatures (200-400°C) under the influence of ultraviolet light. Under these conditions, as noted above, we were able to obtain small amounts of methanesulfonic acid.

By carrying out the sulfoxidation of methane with gaseous sulfur dioxide and oxygen in a flow system in the field of an electrical discharge (duration of the action of the discharge on the reaction mixture varied, in the various experiments, from 1.4 to 4.5 minutes; calculated wavelength 357.6 m), we were able to increase the yield of methanesulfonic acid to 2-3%, based on methane. These experiments were carried out in reactors with an internal electrode in the form of a platinum wire of 0.05 or 0.19 mm diameter. The generator of the high-frequency attenuated vibrations was a "Tesla" transformer with an output of 200 watts at 1,000,000 volts, which was fed by an oil transformer with an output of 1 kw at 10,000 volts.

Analysis of the liquid reaction products established that 1 g of the products contained 0,001145-0,001247 g-equiv. of methanesulfonic acid (10,99-11,97%), 0,005089-0,006261 g-equiv. of sulfuric acid (24,94-30,68%), 0,1-5,5 wt.% methyl alcohol, and the remainder water. We were unable to detect among the reaction products any hydrogen sulfide, mercaptans, carbon disulfide, or carbonyl sulfide. During passage of the gaseous reaction mixture through the zone of the electrical discharge, considerable amounts of sulfur deposited on the walls of the reactors. Formaldehyde, acetylenic hydrocarbons (in amounts of 0,60-0,65 vol. %), carbon monoxide (8,0-12,5%), carbon dioxide (4,8-5,0%), ethylenic hydrocarbons (~0,1%), and hydrogen (14,0-19,0%) were found in the reactor gaseous effluent.

The compositions of the solid, liquid, and gaseous reaction products attest to the great diversity and complexity of the processes occurring among substances in the zone of an electrical discharge. We assume that in the field of a high-frequency electrical discharge, the synthesis of methanesulfonic acid proceeds by a chain mechanism with the intermediate formation of methanepersulfonic acid; however, owing to the great number of different side reactions, which are not considered in this communication, the specific role of the sulfoxidation of methane remains very small. The process which initiates the sulfoxidation of methane is apparently a process of the decomposition of methane molecules, excited by the electrical discharge, in one way or another:

$$CH_4 \rightsquigarrow CH_4^* \rightarrow CH_3^\cdot + H^\cdot \qquad (1)$$

A methyl radical reacts with the sulfur dioxide forming a methanesulfinic radical:

$$CH_3^\cdot + SO_2 \rightarrow CH_3 - SO_2^\cdot , \qquad (2)$$

which is further oxidized by oxygen with the formation of a methanepersulfonic radical:

$$CH_3SO_2^\cdot + O_2 \rightarrow CH_3SO_2O_2^\cdot . \qquad (3)$$

This radical reacts with methane giving a molecule of methanepersulfonic acid and a new methyl radical

$$CH_3SO_2O_2^\cdot + CH_4 \rightarrow CH_3SO_2O_2H + CH_3^\cdot . \qquad (4)$$

The molecule of methanepersulfonic acid is unstable, as are all alkanepersulfonic acids. In aqueous solution, it is very rapidly reduced by sulfur dioxide to methanesulfonic acid with the formation of an equimolar amount of sulfuric acid:

$$CH_3SO_2O_2H + SO_2 + H_2O \rightarrow CH_3SO_3H + H_2SO_4. \qquad (5)$$

The water is formed chiefly by the reactions described by Equations (6), (7), and (13), and also partially by Reaction (10).

$$\left.\begin{aligned} &CH_3^\cdot + O_2 \rightarrow CH_2O + {}^\cdot OH \\ &{}^\cdot OH + CH_4 \rightarrow CH_3^\cdot + H_2O \text{ и т. д.} \end{aligned}\right\} \text{chain} \qquad (6)$$

This scheme agrees with the data of Nalbandyan [9] on the photochemical oxidation of methane in the presence of mercury vapors. Formaldehyde, which was obtained in significant amount under the conditions of our experiments, can be oxidized further by atomic oxygen:

$$HCHO + O^{\cdot} \rightarrow CO + H_2O. \tag{7}$$

The possibility of the formation of methane sulfonic acid by the reaction of methane with radicals formed as a result of the decomposition of the unstable methanepersulonic acid is not excluded:

$$CH_3SO_2O_2H \rightarrow CH_3SO_2O^{\cdot} + {}^{\cdot}OH; \tag{8}$$

$$CH_3SO_2O^{\cdot} + CH_4 \rightarrow CH_3SO_3H + CH_3^{\cdot}; \tag{9}$$

$$CH_4 + {}^{\cdot}OH \rightarrow H_2O + CH_3^{\cdot}. \tag{10}$$

The excess amount of sulfuric acid in the reaction products in comparison with the amount which could have been formed by Reaction (5) was obtained, in all probability, as a result of the following processes:

a) by the reaction of sulfur dioxide with ozone, the formation of which in electrical discharges has already been shown by us experimentally:

$$SO_2 + O_3 \rightarrow SO_3 + O_2; \tag{11}$$

b) by disproportionation of the oxygen in the sulfur dioxide contained in the gaseous reaction mixture, which is accompanied by the simultaneous formation of sulfur [10]:

$$3SO_2 \rightarrow S + 2SO_3; \tag{12}$$

however, the major amount of the sulfur was evidently obtained, all the same, by the reduction of sulfur dioxide by hydrogen [10]:

$$SO_2 + 2H_2 \rightarrow 2H_2O + S; \tag{13}$$

c) by the oxidation of sulfur dioxide by oxygen [10]:

$$2SO_2 + O_2 \rightarrow 2SO_3. \tag{14}$$

As a result of this work, it was established that sulfoxidation of methane by gaseous sulfur dioxide and oxygen takes place in the field of an electrical discharge. The reaction is accompanied by side reactions.

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POLYMERIZATION OF 2-VINYLPYRIDINE AND 2-VINYLQUINOLINE

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(Presented by Academician V. A. Kargin, December 10, 1956)

In spite of the fact that vinyl derivatives of pyridine have recently found widespread use (in the production of SK [synthetic rubber], acrylonitrile fibers, ion-exchange resins, etc.), the process of their polymerization and copolymerization has been little studied [1]. Vinylquinoline is very close in structure to vinylpyridine, but until recently it found only limited application, apparently as a consequence of insufficient knowledge of the polymerization process and of the properties of its polymers [2].

A study of the polymerization of vinyl derivatives of pyridine and quinoline is of theoretical interest, since it permits an evaluation of the effect of the hetero atom in the rings of the vinyl monomers on their behavior in polymerization and copolymerization processes by a comparison with the behavior of their close structural relatives, styrene and vinylnaphthalene. At the same time, it is also possible to study the effect of increased complexity of the molecules of the heterocyclic monomer, caused by the fusion of a second benzene ring, on the polymerization and copolymerization processes.

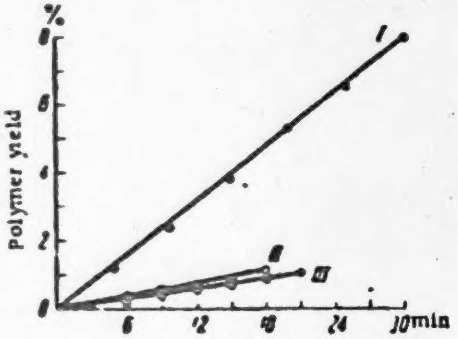
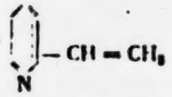
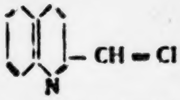


Fig. 1



2-vinylpyridine



2-vinylquinoline

With this aim, we synthesized 2-vinylpyridine and 2-vinylquinoline by reaction of picoline and quinaldine with paraformaldehyde and subsequent dehydration of the resulting carbinols over potassium hydroxide. The physical properties of the monomers are presented in Table 1.

In order to study the polymerization reactivity of 2-vinylpyridine and 2-vinylquinoline, we studied the kinetics of the bulk polymerization of these monomers by a dilatometric method in the presence of 0.135 mol. % of the azodinitrile of isobutyric acid [2-azobisisobutyronitrile] at 50, 55, 60, 75, and 90°. The apparatus for filling the dilatometric ampoules consisted of a distillation flask, a condenser, and a receiver-desiccator which were placed the ampoules containing weighed portions of the initiator. Distillation of the monomers into the ampoules was carried out in a stream of specially purified nitrogen, which guaranteed highly reproducible results.

Moreover, the bulk copolymerization of 2-vinylpyridine and 2-vinylquinoline with styrene, isoprene, and chloroprene was studied at 60° in the presence of 0.2 wt. % 2-azobisisobutyronitrile. The amount of

TABLE 1

Physicochemical Properties of the Monomers

Monomer	B. p. °C/mm		Refractive index n_D^{20}		d_4^{20}		MR			Elemental composition, %					
										C		H		N	
	found	Lit. [6]	found	Lit. [5]	found	Lit. [7]	found	Lit. [6]	calc.	found	calc.	found	calc.	found	calc.
2-vinylpyridine	64.5/20	60/17	1.5497	1.5495	0.9757	0.9770	34.33	34.40	33.60	80.02	80.0	6.85	6.66	13.16	13.33
2-vinylquinoline	104/3	120-125/7	1.6485	1.6439	1.0705	1.0692	52.70	—	51.14	85.50	85.15	6.00	5.80	9.19	9.03

copolymer formed was determined after threefold recoagulation and drying at 40° under vacuum to constant weight. The composition of the copolymers was determined by analysis for nitrogen by the Dumas micromethod. The copolymerization rate constants were determined using the integral equation of copolymer composition according to the method of G. A. Shtraikhman [3].

As seen from Figure 1, 2-vinylpyridine (Curve I), in contrast to 2-vinylquinoline (Curve II), polymerizes very readily, beginning at a temperature of 50°.

The monomers studied can be arranged in the following series according to polymerization rate: 2-vinylpyridine (I) >> 2-vinylquinoline (II) > styrene (III). The activation energies for the polymerization of 2-vinylpyridine and 2-vinylquinoline were obtained from the study of the reaction kinetics:

Monomer	k_0, sec^{-1}	u, kcal /mole
2-vinylpridine	$1 \cdot 10^9$	20.4 ± 1.4
2-vinylquinoline	$1 \cdot 10^9$	18.3 ± 1.3

The slow polymerization of 2-vinylpyridine was unexpected, and was apparently due to steric hindrance occurring during the reaction of radical with monomer.

A comparison of the activation energies of 2-vinylpyridine and ?-vinylquinoline with thos of styrene those (21.5 kcal /mole) and 2-vinylnaphthalene (18.8 kcal./mole) indicates that increasing the complexity of the molecule of the vinyl compound by introducing a second benzene ring leads to an increase in reactivity of the monomer owing to an increase in the number of conjugated double bonds [4].

For a more complete characterization of the reactivity of the 2-vinylpyridine and 2-vinylquinoline monomers, we studied their copolymerization with a number of monomers, and determined the values of the two copolymerization rate constants r_1 and r_2.

From the data presented, it follows that: 1) 2-vinylquinoline is more active in copolymerization processes than 2-vinylpyridine; 2) 2-vinylpyridine and 2-vinylquinoline are more active than styrene.

Monomer M_1	Monomer M_2	r_1	r_2
2 Vinylpyridine	styrene	1.81 ± 0.05	0.55 ± 0.09
	isoprene	0.48 ± 0.07	0.53 ± 0.05
	chloroprene	0,094 ± 0.001	5.105 ± 0.003
2-vinylquinoline	styrene	2.69 ± 0.55	0.40 ± 0.14
	isoprene	1,882 ± 0.003	0,534 ± 0.001
	chloroprene	0.38 ± 0.08	2.10 ± 0.17

Thus, it was shown that the introduction of a nitrogen heteroatom into the aromatic ring of a vinyl monomer and also an increase in the number of condensed benzene rings in the monomer increase the reactivity of vinyl monomers.

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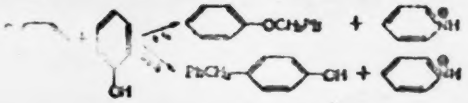
INVESTIGATION OF THE MECHANISM OF THE ALKYLATION OF PHENOLS BY N-TRIMETHYL-α-PHENETHYLAMMONIUM IODIDE

Corresponding Member Acad. Sci. USSR, D. N. Kursanov and S. V. Vitt

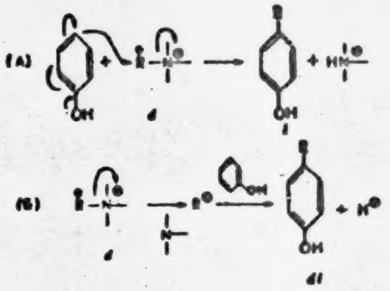
The alkylation of phenols and phenolate anions by ammonium compounds containing a benzyl or substituted benzyl radical has been studied by a number of authors [1-3].

It has been established [4] that a mixture of products of C- and O-alkylation is formed by the reaction of N-benzylpyridinium chloride with phenol:

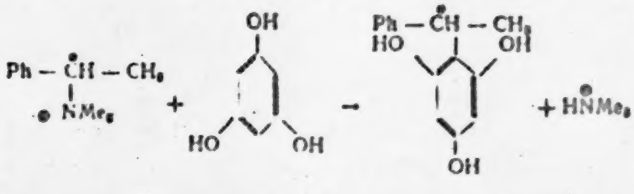


It may be supposed, then, that this reaction, similarly to previously studied [5-8] alkylations by ammonium salts, is a heterolytic substitution reaction of the S_N-type.

The alkylation of phenols by ammonium salts can proceed by either a synchronous mechanism (A) or an asynchronous mechanism (B) which includes the intermediate formation of a carbonium ion [8]



We investigated the reaction of N-trimethyl-α-phenethylammonium iodide with resorcinol and phloroglucinol. It was found that on heating these phenols with the ammonium salt, substitution of the hydrogen atoms of the phenol nucleus by an α-phenethyl group (a C-alkylation reaction) occurred:

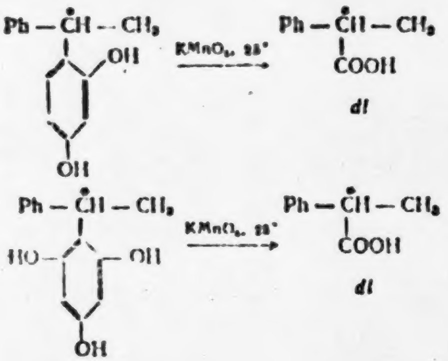


This reaction proceeds readily at a temperature of 150° and above.

The alkylation of resorcinol and phloroglucinol by optically active N-trimethyl-α-phenethylammonium iodide was carried out at 155-175° in an excess of the alkalatable phenol.

In this instance, if the reaction proceeds according to Scheme (A), the α-phenethylphenols formed must be optically active; if the reaction proceeds according to Scheme (B), they will be inactive.

It was found that the α-phenethylphenols formed in this reaction do not possess optical activity.* Nor did the α-phenylpropionic acid, obtained by oxidation of the phenols, possess optical activity:



These data permit the conclusion that the alkylation of the phenols by N-trimethyl-α-phenethylammonium salts proceeds in such a manner that the initially formed ammonium ion decomposes with the formation of an α-phenethyl carbonium ion, which then reacts with the phenol; i. e., the reaction proceeds according to Scheme (B).

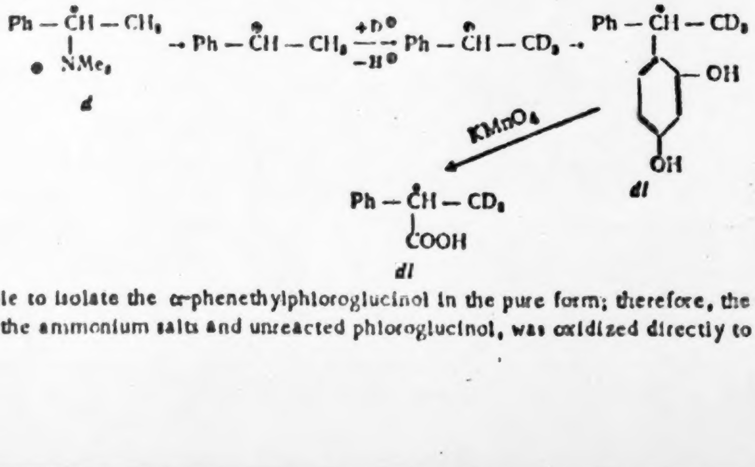
This conclusion with respect to the mechanism of the reaction found further confirmation in the following.

A reaction was carried out between N-trimethyl-α-phenethylammonium iodide and deuteroresorcinol. In this case, the deuteroresorcinol was not only the object of alkylation, but also served as a deuterium donor. The α-phenethylresorcinol formed contained a certain amount (from 6 to 10% of the calculated amount) of deuterium in the phenethyl group.

These figures were obtained from isotope analysis of the water from the combustion of α-phenylpropionic acid — the product of the mild oxidation of deutero-α-phenethylresorcinol.

Carbonium ions possess proton mobility, and, in the presence of deuterium donors, exchange hydrogen atoms from the carbon atom next to the carbonium center [9].

This property of carbonium ions permits judgement as to their part in chemical conversions. Therefore, the formation of α-phenethylresorcinol containing deuterium in the phenethyl group indicates the intermediate formation of an α-phenethyl carbonium ion:



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* We were unable to isolate the α-phenethylphloroglucinol in the pure form; therefore, the reaction mixture, after removal of the ammonium salts and unreacted phloroglucinol, was oxidized directly to α-phenylpropionic acid.

The slight depth of exchange percentage-wise (but significant in absolute value) apparently indicates a short life for the α-phenethyl carbonium ion. From the data on the depth of exchange, it follows that the rate of the deuterium-exchange reaction of the α-phenethyl ion is at least ten times less than the rate of the reaction of this ion with resorcinol.

EXPERIMENTAL

1. Reaction of d-N-trimethyl-α-phenethylammonium iodide with resorcinol. A mixture of 0.1 mole of d-N-trimethyl-α-phenethylammonium iodide [8] and 0.2 mole of resorcinol was heated in an atmosphere of nitrogen for 6 hours at 175 ± 2°.

The reaction products were treated with water and extracted with ether.

The ether solution was extracted with 4 N NaOH, and the resulting alkaline solution was acidified with sulfuric acid.

The liberated oil was extracted with ether and dried with magnesium sulfate. The residue remaining after evaporation of the solvent was fractionated with a herringbone dephlegmator of 8-cm height. This yielded α-phenethylresorcinol with a b.p. of 189-192° (2 mm). The material crystallized on standing. The colorless needles resulting from recrystallization from n-hexane–benzene mixture melted at 78.0-79.0°. The substance did not possess optical activity.

Found %: C 78.47; H 6.55 $C_{14}H_{14}O_2$. Calculated %: C 78.51; H 6.59

The bis-p-nitrobenzoate, recrystallized from n-hexane–benzene mixture, melted at 143.5-144°.

2. Oxidation of α-phenethylresorcinol to α-phenylpropionic acid. The reaction was carried out under the conditions described by Hart [10].

To a solution of 4.57 g of α-phenethylresorcinol in 350 ml of acetone was added, with stirring, a solution of 25.6 g of $KMnO_4$ in 1.2 liters of water cooled to 10-12°. The rate of the addition of the solution was regulated so that the temperature of the reaction mixture remained in the range 24-26°. After the addition of all of the permanganate solution, stirring was continued for 30 minutes, after which the reaction mixture was carefully acidified with 4 N sulfuric acid, and a solution of sodium bisulfite was added to dissolve the precipitated manganese dioxide.

The reaction mixture was extracted with methylene chloride, and the extract was washed with water and then extracted with a 2 N solution of soda. After filtration, the alkaline solution was acidified with 4 N sulfuric acid. The liberated acid was extracted with methylene chloride, and the extract was dried with $MgSO_4$.

After removal of the solvent, the α-phenylpropionic acid was distilled. Yield 1.34 g, b.p. 147-149° (14 mm) (after two distillations), n_D^{22} 1.5228 (according to literature data [10], α-phenylpropionic acid has a b.p. of 145-8° (15 mm), n_D^{20} 1.5210). The acid obtained was optically inactive ($[\alpha]_D^{20}$ 0 ± 0.2°).

Neutralization equivalent: found 150.6; calculated 151.1.

Found %: C 71.46; H 6.65 $C_9H_{10}O_2$. Calculated %: C 71.97; H 7.71

S-Benzylthiuronium salt m.p. 143-144°.
p-Bromophenacyl ester m.p. 62-63°.

Found %: C 59.22; H 4.14 $C_{17}H_{15}O_3Br$. Calculated %: C 58.91; H 4.35

3. Reaction of dl-N-trimethyl-α-phenethylammonium iodide with deuteroresorcinol. 27.5 g of resorcinol and 6.0 ml of deuterium oxide were placed in a distillation flask. The contents of the flask were equilibrated by mild heating. The water was distilled under vacuum and collected in a receiver cooled with liquid nitrogen. After removal of all of the water, the deuteroresorcinol was distilled. B.p. 163-6° (17 mm). Yield 26.8 g.

The water obtained from combustion of the deuteroresorcinol had an excess density of 18,600 γ/ml.

A mixture of 29.1 g of dl-N-trimethyl-α-phenethylammonium iodide and 18.5 g of deuteroresorcinol was heated under nitrogen at 172 ± 2° for 3 hours. 8.42 g of deutero-α-phenethylresorcinol was obtained, b.p. 197-8° (4 mm), m.p. 77.5-78.5° (from a mixture of benzene and n-hexane). 7.13 g of deutero-α-phenethylresorcinol was oxidized to α-phenylpropionic acid. There was obtained 1.55 g of a substance with a b.p. of 154-6° (18 mm), n_D^{20} 1.5229.

The water obtained by combustion of a α-phenylpropionic acid had an excess density of 416 γ/ml, which comprises 9.6 % of the value calculated for equilibrium.

The introduction of deuterium into the phenethyl group is evidence for the formation of an α-phenethylcarbonium ion during the alkylation of resorcinol by the ammonium salt.

4. Reaction of d-N-trimethyl-α-phenethylammonium iodide with phloroglucinol. A mixture of 0.03 mole of d-N-α-trimethyl-α-phenethylammonium iodide and 0.04 mole of phloroglucinol was heated under nitrogen for 6 hours at 155 ± 1°.

The reaction mixture was treated with 30 ml of 0.5 N H_2SO_4 and 30 ml of ether. The phloroglucinol was filtered, and the ether solution was washed with water and dried with $MgSO_4$.

Removal of the solvent by distillation left a thick, uncrystallizable residue (5.75 g).

Since attempts to isolate pure α-phenethylphloroglucinol from this residue were unsuccessful, it was oxidized directly to α-phenylpropionic acid. This gave 1.64 g of α-phenylpropionic acid, b.p. 143-6° (12 mm), n_D^{26} 1.5210.

Investigation of the specific rotation showed that the substance was completely devoid of optical activity ($[\alpha]_D^{20}$ 0 ± 0.2°). From this, it follows that the α-phenethylphloroglucinol was also optically inactive.

In a similar experiment, from 29.0 g of dl-N-trimethyl-α-phenethylammonium iodide and 17.3 g of phloroglucinol was obtained 6.21 g of dl-α-phenylpropionic acid, b.p. 159-160° (20 mm), n_D^{21} 1.5225.

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RECRYSTALLIZATION DIAGRAM OF MOLYBDENUM

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As is well known, along with other factors, grain size has an effect on the mechanical properties of metals. Molybdenum is among the metals to which this particularly applies: by means of properly selected mechanical and thermal treatment to give a fine-grained, uniform structure, brittle, coarse-grained molybdenum castings become much more plastic and can be subjected to cold deformation.

Consequently, the construction of the recrystallization diagram of molybdenum, relating the grain size of the metal with degree of deformation and annealing temperature, is of particularly great interest.

Data are available in the literature on the dependence of the recrystallization temperature of molybdenum of different grades on mechanical and thermal treatment [1, 4], but a systematic study of the recrystallization diagram has not been carried out.

We constructed the recrystallization diagram of the first type for molybdenum which had been cast in an arc furnace under vacuum and reduced by carbon. Chemical and gas analysis showed that the molybdenum contained 0.2-0.1% carbon, a few hundredths of a per cent of iron, and traces of silicon. The oxygen content was ~ 0.002%.

In order to obtain a uniform, fine initial structure, the molybdenum castings were forged in several steps. The temperature at the beginning of the forging was 1600° and at the end, 1300°. Heating of the samples before forging was carried out in a hydrogen furnace. The total degree of deformation was 90%. As a result of this treatment at high temperatures, the very coarse, nonuniform casting structure was eliminated; forging at the lower temperature (below the recrystallization temperature of the molybdenum) was continued to the formation of texture. After annealing of the deformed samples for 1 hour under vacuum at 1300° (this annealing regime was selected as a result of experiments), the samples had a polyhedral, fine-grained structure with an average grain diameter of about 22-25 μ.

For construction of the recrystallization diagram, the initial samples, obtained by the above-described method, were subjected to cold deformations with degrees of set of 2.5, 5, 7.5, 10, 20, 30, 40, 50, 60, and 70% by compression in a 35-ton hydraulic press. In order to obtain the specified dimensions, the compression was carried out in limiting rings, the height of which corresponded to the required final dimension. Failure of the samples during this treatment was not observed, and only on an increase in the degree of deformation above 20% was there observed small cracks at the edges, while attempts to deform the molybdenum castings led to considerable splitting even at low degrees of deformation. Investigation of the microstructure of the initial samples after cold deformation showed that at low degrees of deformation (2.5, 5, 7.5%) oriented blocks of grains appeared, grain crushing was observed at higher degrees, and a reduction of above 50% led to the formation of elongated, parallel threads in the direction of compression (Figures 1a, b, and c).

The deformed samples were annealed for 1 hour under vacuum (10^{-5}) at 1100, 1200, 1300, 1400, 1530, and 1730°. Microstructure analysis was carried out on the annealed samples, and the microhardness and hardness of the deformed and annealed samples were measured.

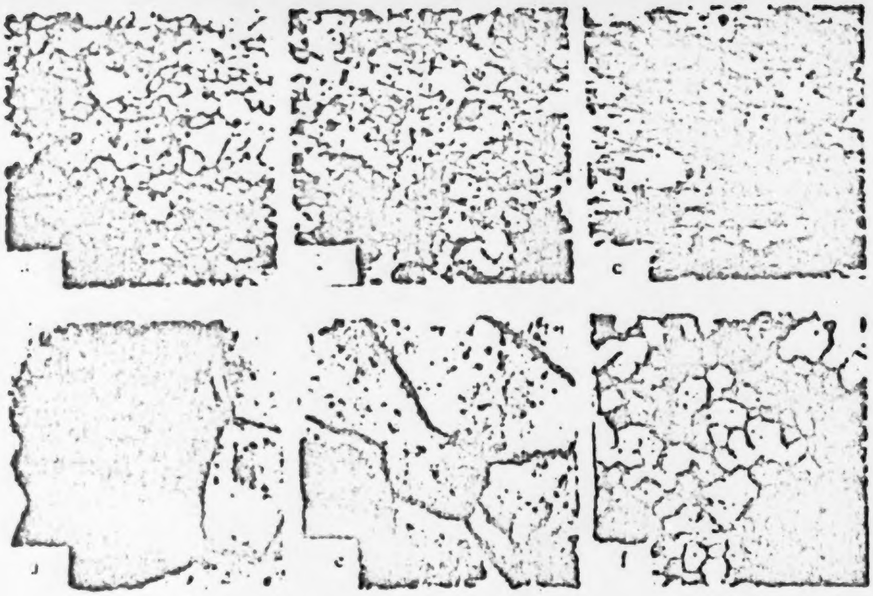

Fig. 1. Microstructure of the initial samples of molybdenum after cold deformation and and annealing (100 x): a) 7.5% compression, b) 30% compression, c) 70% compression, d) same as a after annealing at 1530°, e – 2.5% compression and annealing at 1730°, f – same as c after annealing at 1730°.

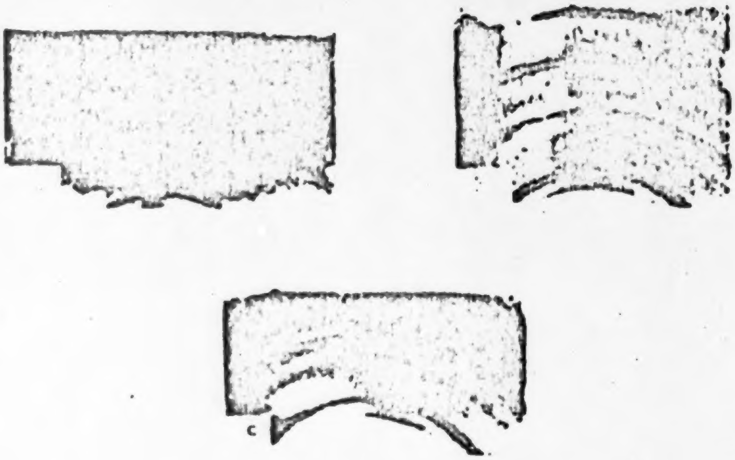

Fig. 2. x-Ray photographs of molybdenum: a) initial, b) 70% deformation, c) 70% deformation and annealed at 935°.

Determination of the temperature of the beginning of recrystallization was by the x-ray method, and, for the increased precision in this determination, additional annealing was carried out at temperatures of 935, 950, 960, 970, 980, 985, 1000, 1010, 1025, 1030, 1040, 1050, 1070, and 1180°. A solution of nitric and sulfuric acids in water (5 parts HNO_3, 1 parts H_2SO_4, 3 parts H_2O) was used as the etcher to develop the microstructures. Average grain size was determined under the microscope by the intersection method and by calculating the grain surface on photomicrographs in order to evaluate the effect of degree of deformation and annealing temperature on grain size.

The x-ray exposures were by molybdenum radiation with an exposure time of 1.5-2 hours. On the basis of these investigations, it was established that recrystallization begins at 955° for molybdenum samples 70% cold-deformed (Figure 2) and at 1025° at 50% deformation. At lower degrees of deformation (10%), recrystallization begins only at 1200°.

Above 1300°, recrystallization was observed in all deformed and annealed samples. Grain growth at the critical degree of deformation occurred from 1400° (10% deformation). An increase in temperature led to still more intense grain growth, maximum grain size being observed at 7.5% deformation for 1530° and at 2.5% deformation for 1730°, while at higher deformations and the same annealing temperature (1530°, 70%) grain size was considerably less (Figure 1, d, e, f). Hardness measurement was carried out with a 100-kg load on the cone penetrator; microhardness was measured with a diamond point at a load of 50 g. It is curious that the above-mentioned formation of a block structure was always accompanied at low compressions by a decrease in the hardness of the samples. The hardness and microhardness then increased with an increase in deformation. An especially strong increase in hardness was observed at 10% deformation. Subsequent annealing considerably decreased the hardness of the samples. Thus, at a deformation of 70% the hardness was about 220 kg/sq. mm, and after annealing at 1100° it decreased to 187 kg/sq. mm owing to the occurrence of recrystallization. An increase in annealing temperature to 1730° still further decreased the hardness of the sample (to 157 kg/sq. mm), which was caused by an increase in the recrystallized grains (Table 1). The presence of a "critical" degree of deformation caused a certain decrease in hardness, which was especially noticeable at high annealing temperatures. The change in microhardness in relation to degree of deformation and annealing temperature was similar to the change in over-all hardness of the sample with the difference that higher values of hardness were observed in this case.

TABLE 1

Hardness of Deformed and Annealed Molybdenum Samples (kg/sq. mm)

Annealing temperature, °C	Deformation, %										
	0	2.5	5	7.5	10	20	30	40	50	60	70
Deformed, not annealed	171	166	170	172	178	182	189	192	201	205	220
1100	168	162	163	164	173	173	173	173	178	178	187
1200	166	163	166	170	175	175	175	171	177	177	183
1300	165	163	164	169	169	171	172	172	172	174	176
1400	163	160	163	161	168	167	167	167	167	168	165
1530	162	158	162	159	164	160	160	158	158	158	160
1730	154	142	152	156	157	156	156	152	155	157	157

On the basis of these investigations, we constructed the recrystallization diagram of molybdenum (Figure 3). The variation in the temperature at which recrystallization begins with the degree of deformation is shown on the diagram as a broken line. From the data of the diagram, it is seen that grain growth was not observed on annealing of the cold-deformed molybdenum samples up to 1300°, and the grain dimensions were commensurate with the dimensions of the initial grains at all degrees of deformation: the average grain diameter of the initial samples annealed to 1300° was about 20-23 μ, for deformed samples annealed at this same temperature it did not exceed 30-32 μ, and at high degrees of deformation the average grain size decreased to 20 μ. Annealing at 1400° led to appreciable grain growth at a deformation of 10%.

Above 1400° coarsening of the grains was observed at all degrees of deformation, the "critical" degree of deformation shifted to 7.5%, and the average grain diameter increased at 1600° to 223 μ. There was considerably less grain growth at high degrees of deformation (beginning at 40%), and at 70% it was only 40 μ.

Annealing at 1700° led to still more grain growth. At this annealing temperature, the "critical" degree of deformation shifted to 2.5%, and the grain size increased to 300 μ. The average grain diameter of samples deformed by more than 20% was 80-90 μ, and it did not change with an increase in the degree of deformation.

On the basis of this set of data obtained during the investigation of the recrystallization of molybdenum, it can be concluded that hot-worked molybdenum, after cold working at deformation above 20%, can be annealed up to 1400°. The grain size will remain small during this treatment.

Higher annealing temperatures lead to a coarse-grained structure after annealing.

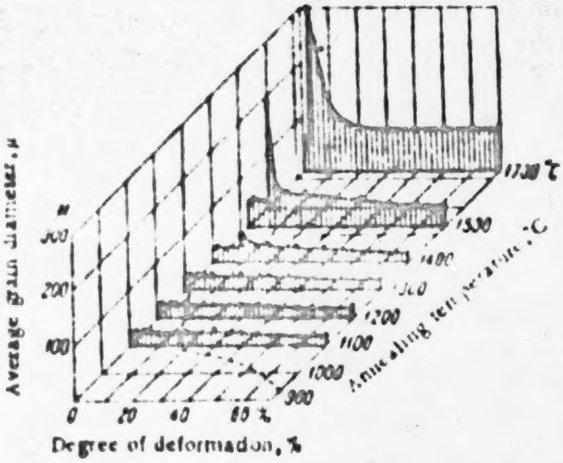

Fig. 3. Recrystallization diagram of the first type for molybdenum.

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ON THE COMPLEX COMPOUNDS OF LANTHANUM, CERIUM, PRASEODYMIUM, AND NEODYMIUM WITH THIOUREA

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The ability of thiourea to form complex compounds with salts of various metals is very well developed. Thus, Reinolds [1], who discovered thiourea by isomeric conversion of ammonium thiocyanate, pointed out its ability to form compounds with metal salts. He prepared and described characteristic compounds with gold and platinum chlorides. then, a number of investigators [2-7] prepared numerous compounds of thiourea with salts of lead, cadmium, mercury, tin, bismuth, thallium, tellurium, copper, cobalt, zinc, iron, nickel, and other metals.

Large-scale investigations in the field of complex compounds of silver, platinum, and palladium with thiourea, its alkyl derivatives, and other sulfur-containing organic substances related to it were carried out by N. S. Kurnakov [8].

Further, compounds of this type were studied by L. N. Chugaev [9], V. V. Lebedinsky and coauthors [10], and others.

Considering the clearly expressed ability of thiourea to form complex compounds with metal salts, it was not without interest to carry out research on the preparation and study of similar compounds with salts of the rare-earth elements of the cerium group.

The starting materials for the preparation of complex compounds of the rare-earth elements with thiourea were the anhydrous acetates and thiourea with m.p. of 180-182°.

It was first established that the acetates of lanthanum, cerium, praseodymium, and neodymium combine with urea in aqueous medium to give several products, the formation of which depends on the relative amounts and temperature of the reacting substances. The most stable complex compounds of these elements in aqueous medium are those in which, according to analytical data, there is one atom of rare-earth element per molecule of thiorea. These compounds were studied by us first.

These compounds were prepared by mixing aqueous solutions of the acetates of the rare-earth elements with an excess of thiourea, specifically in a molar ratio of 1:2 (anhydrous metal acetate to thiourea), in neutral or slightly acid medium (several drops of acetic acid were added) with subsequent removal of the excess solvent.

A weighed portion of lanthanum, cerium, praseodymium, or neodymium acetate was dissolved in the least possible amount of water at a temperature not above 30-40°, and into this solution was introduced the dry thiourea in an amount calculated according to the ratio indicated above. The excess solvent was then evaporated at room temperature in a vacuum desiccator over calcium chloride or by heating at not above 55°. After some time, well-formed, coarse, lustrous, highly refractive crystals separated from the solution in the form of thick, short prisms, colorless in the case of lanthanum and cerium, green in the case of praseodymium, and lilac in the case of neodymium. Separated by vacuum filtration from the mother liquor, the crystals were quickly washed with a small amount of cold water and dried in air until they lost the ability to adhere to the walls of the beaker. Dehydration of the compounds was then continued in a vacuum desiccator over calcium chloride and phosphorus anhydride, but no loss in weight was observed. However, these compounds contained water of crystallization, which was slowly, and with difficulty removed in a constant temperature cabinet.

Thus, the lanthanum and cerium compounds lost their water of crystallization at 105-110°, the analogous compound of praseodymium – at 130-140°, and neodymium – at 155-160°.

The compounds obtained were stable in water, and easily crystallized well from the latter without a change in their chemical composition. They had a definite melting point, which was 258-260° for the lanthanum complex, and 225-226°, 292-293°, and 297-298° for, respectively, the analogous compounds of cerium, praseodymium, and neodymium. The complex compounds of these elements melted with decomposition at the indicated temperatures.

Two-fold recrystallization of the compounds from water did not change their melting points. Yield of the compounds was close to theoretical, 98-99%.

The complex compounds of lanthanum, cerium, praseodymium and neodymium with thiourea are highly soluble in cold and hot water, methyl alcohol, and aniline; they are more difficultly soluble in ethyl alcohol, pyridine and quinoline; they are practically insoluble in ether, acetone, benzene, toluene, xylene, dichloroethane, chloroform, and isoamyl and isobutyl alcohols. In addition to the organic solvents indicated above, these complexes are highly soluble in dilute and 80% acetic acid and in hydrochloric and sulfuric acids; concentrated nitric acid in the cold, or dilute acid with heating, decomposes them with the liberation of nitrogen oxides.

The preliminary ob[illegible] that, apparently, practical interest centers in the study of the relative solubility of these compounds in water, methyl and ethyl alcohols, pyridine, and quinoline.

The analyses of the dehydrated complex compounds for content of rare-earth elements, with the exception of praseodymium, were carried out by precipitation as the oxalates and subsequent conversion to the oxides by calcination. The sulfur was determined as barium sulfate. Nitrogen was determined by the Dumas method, and carbon and hydrogen by elemental organic analysis.

Complex Lanthanium Salt

Hydrated Salt

Found %: H_2O 8.63, 8.61. $La(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot 2H_2O$. Calculated %: H_2O 8.42.

Anhydrous Salt

Found %: La 35.39, 35.65; S 8.02, 8.20; C 21.57, 21.34; H 3.27, 3.61; N 7.13, 7.04. $La(C_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated %: La 35.42; S 8.17; C 21.44; H 3.33; N 7.14.

Complex Carium Salt

Hydrated Salt

Found %: H_2O 8.02, 8.29. $Ce(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot 2H_2O$. Calculated %: H_2O 8.29.

Anhydrous Salt H

Found %: Ce 35.5, 35.56; S 8.40, 8.69; C 21.98, 21.25; H 3.10, 3.40; N 7.30, 7.50. $Ce(C_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated %: Ce 35.56; S 8.14; C 21.33; H 3.30; N 7.12.

Complex Praseodymium Salt

Hydrated Salt

Found %: H_2O 4.46, 4.40. $Pr(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot H_2O$. Calculated %: H_2O 4.36.

Anhydrous Salt

Found %: S 8.30, 8.50; C 21.68, 21.73; H 3.94, 3.64; N 7.55, 7.60. $PrC_2H_3O_2)_3 \cdot CS(NH_2)_2$. Calculated %: S 8.10; C 21.28; H 3.40; N 7.13.

Complex Neodymium Salt

Hydrated Salt

Found %: H_2O 4.34, 4.51. $Nd(C_2H_3O_2)_3 \cdot CS(NH_2)_2 \cdot H_2O$. Calculated %: H_2O 4.33.

Anhydrous Salt

Found %: Nd 36.10, 36.28; S 8.05, 8.52; C 21.33, 21.48; H 3.84, 3.52; N 7.41, 7.60. $Nd(C_2H_3O_2)_3 \cdot CS(NH_2)_2$.
Calculated %: Nd 36.22; S 8.059; C 21.02; H 3.26; N 7.04.

The anhydrous complex compounds of lanthanum, cerium, praseodymium, and neodymium with thiourea did not display any difference in behavior or properties in comparison with the corresponding crystalline hydrates.

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ALKYLATION OF ISOPENTANE WITH PROPYLENE AND ISOBUTYLENE IN THE PRESENCE OF A SERIES OF PHOSPHORIC ACIDS CONTAINING FLUORINE AND BORON TRIFLUORIDE

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The catalytic alkylation of isoparaffins with olefins has now found widespread industrial use for the production of isoparaffins – high octane components of motor fuel.

Sulfuric acid, boron trifluoride, aluminum chloride and a number of compounds of boron trifluoride with inorganic acids are usually used as catalysts for this reaction.

The authors of the present paper studied the alkylation of isopentane with propylene and isobutylene in the presence of monofluorophosphoric and difluorophosphoric acids saturated with boron trifluoride. For comparison, experiments were also carried out using as the catalyst orthophosphoric acid saturated with boron trifluoride.

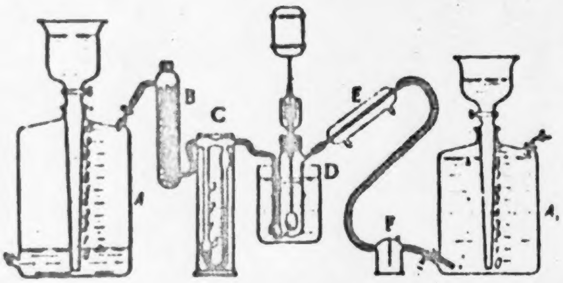

Fig. 1. Apparatus for the alkylation of isopentane with olefins.

The experiments were carried out in the apparatus shown in Figure 1. Olefin from container A was fed at a rate of 2 liters/hour through the calcium chloride tube to reactor D. The olefin rate was measured with flow meter C. The unreacted gas passed through condenser E and trap F, and was collected in container A_1. Stirring of the isopentane, olefin, and catalyst was accomplished by means of a high-speed loop stirrer which entered the reactor through a mercury seal. The isopentane used in the experiments had a boiling point of 27-28°, a density (d_4^{20}) 0.6196 and an index of refraction (n_D^{20}) 1.3562.

In order to obtain an idea of the activity of the various catalysts in the alkylation of isopentane with propylene, a series of experiments was carried out to determine the catalyst life of these catalysts.

In each experiment was used 15 ml of catalyst, 54 g of isopentane, and 9 liters of propylene, which corresponded to a molar ratio of isopentane to propylene of approximately 2 : 1. The experiments were carried out at room temperature.

At the conclusion of an experiment, the alkylation products were decanted from the catalyst, and the catalyst was used in the following experiment.

In Figure 2 is shown the stability of the activity of the catalysts in the alkylation of isopentane with propylene. The most active of the catalysts studied in the alkylation of isopentane with propylene was monofluorophosphoric acid saturated with boron trifluoride, and the least active was orthophosphoric acid saturated with boron trifluoride. In fact, in the alkylation of isopentane with propylene, in the case of monofluorophosphoric acid saturated with boron trifluoride 35 volumes of alkylate were formed per volume

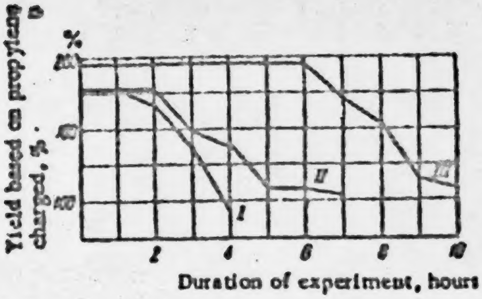

Fig. 2. Catalyst life for the series of catalysts during the alkylation of isopentane with propylene. I) $H_3PO_4 \cdot BF_3$, II) $HPO_2F_2 \cdot {}^1/_2BF_3$, III) $H_2PO_3F \cdot BF_3$.

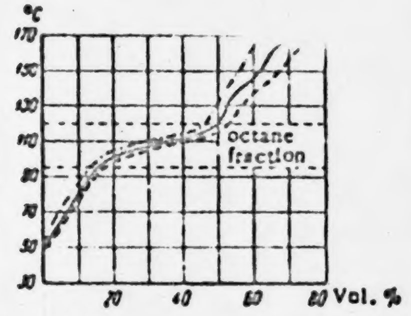

Fig. 3. Fractional composition of the alkylates produced from isopentane and propylene with the various catalysts. See Figure 2 for notation.

of catalyst, while in the case of difluorophosphoric acid and orthophosphoric acid saturated with boron trifluoride, 15.8 and 9.2 volumes of alkylate, respectively, were formed.

The alkylates were fractioned in a column with a separation effectiveness of 40 theoretical plates. Distillation curves for the alkylates from the alkylation of isopentane with propylene are shown in Figure 3. As seen from the curves, with a decrease in catalytic activity of the catalysts, the alkylates contained significantly less of the fraction boiling to 170°. For example, in the case of the alkylation of isopentane with propylene in the presence of orthophosphoric acid saturated with boron trifluoride the total of the fractions boiling to 170° was 65.4%, while when monofluorophosphoric and difluorophosphoric acids saturated with boron trifluoride were used as the catalysts these fractions totaled 77.9 and 70.8%, respectively.

The fractions of the alkylates boiling to 170° did not contain unsaturated compounds. The latter were observed, in small amounts, only in the residues from the distillations of the alkylates. The content of unsaturated compounds in the residues from the distillations of the alkylates increased with a decrease in catalyst activity. For example, the residue from the distillation of the alkylate obtained in the presence of monofluorophosphoric acid saturated with boron trifluoride had a bromine number of 0.8, while the bromine number of the residue from the distillation of the alkylate obtained in the presence of orthophosphoric acid saturated with boron trifluoride was 8.

As seen from Figure 3, in the alkylation of isopentane with propylene there was formed a large amount of fractions boiling below the boiling range of the isooctane fraction, and with an increase in catalyst activity, the amount of these fractions increased somewhat. For example, in the experiments on the alkylation of isopentane with propylene in the presence of the most active of the catalysts studied – the molecular compound of monofluorophosphoric acid with boron trifluoride – there was formed 16% of these fractions. In experiments carried out under the same conditions in the presence of difluorophosphoric and orthophosphoric acids saturated with boron trifluoride, the fractions boiling below the isooctane boiling range amounted to 15.6 and 12.5%, respectively.

Moreover, during the alkylation of isopentane with propylene there were also formed isoparaffins with a greater number of carbon atoms than isooctanes but with a smaller number of carbon atoms than in isoparaffins which would be formed as the result of polyalkylation.

The formation of by-product isoparaffinic fractions, along with the basic hydrocarbons, is explained by a certain degree of reversibility of the catalytic alkylation reaction. This is confirmed by the observations of Birch and Dunstan [1], who established that 2,3 dimethylbutane, 2,2,4-, 2,2,3-, and 2,3,3-trimethylpentanes, and 2,2,5-trimethylhexane decompose on stirring with sulfuric acid at 15-20°, forming a mixture of isoparaffins of higher and lower molecular weight.

According to the data of Mamedaliev and Nagiev [2], 2,2,4- and 2,2,3-trimethylpenylpentanes are cleaved by lengthy stirring with 97% sulfuric acid at room temperature, forming, along with liquid hydrocarbons, a mixture of iso- and normal butanes. On distillation of the isooctane which had been treated with sulfuric acid, about 20% of the product boiled up to 99° and about 30% boiled above 120°, i.e., outside the boiling range of the isooctane fraction.

Thus, the formation of fractions containing hydrocarbons with a lower number of carbon atoms than the expected product is explained by the fact that isoparaffins with a branched carbon atom chain are insufficiently stable under catalytic alkylation conditions. As a result, dealkylation of the isoparaffins formed takes place, forming isoparaffins and olefins of different structure than those used in the reaction if the bond between carbon atoms is ruptured in a place other than that involved in the formation of the isoparaffin. By a second alkylation of this new isoparaffin, hydrocarbons are obtained with a higher molecular weight than that of the basic product, but with a lower molecular weight than that of polyalkylate.

The octane fractions of the isopentane-propylene alkylates obtained in the presence of the catalysts studied (the 95-110° and 110-120° fractions) were analyzed by Raman spectra. It was established that the octane fractions of the isopentane-propylene alkylates, independently of the catalyst used, consisted of a mixture of three isomers: 2,3-, 2,4-, and 2,5-dimethylhexanes.

During the alkylation of isopentane with isobutylene, the same regularities were observed as in the alkylation of isopentane with propylene. Both during the alkylation of isopentane with propylene and during the alkylation of isopentane with isobutylene, with a decrease in catalyst activity there was a decrease in alkylate yield, an increase in bromine number, index of refraction, and density of the alkylate, and a decrease in the content of the lighter fractions boiling up to 170°.

For example, in the alkylation of isopentane with isobutylene in the presence of monofluorophosphoric acid saturated with boron trifluoride, at a molar ratio of isopentane to isobutylene of 2 : 1, there was obtained 71.0% of a fraction distilling up to 170°. When using as the catalyst difluorophosphoric or orthophosphoric acid saturated with boron trifluoride, 68.2% and 65.2%, respectively, of these fractions were obtained.

The density and index of refraction of the same fractions of isopentane-isobutylene alkylates obtained with the various catalysts differed little from each other. In addition, these constants were close to the constants of isoparaffinic hydrocarbons boiling in these same ranges. Consequently, as in the case of the alkylation of isopentane with propylene, the alkylate fractions obtained by us consisted of isoparaffinic hydrocarbons. In the residue from the distillation, along with isoparaffinic hydrocarbons, there were unsaturated compounds, the amount of which increased with a decrease in catalyst activity. In general, the content of unsaturated compounds in the isopentane-isobutylene alkylates was greater than in the isopentane-propylene alkylates. This is explained by the fact that isobutylene polymerizes considerably more readily than propylene.

The formation of isononanes can be expected from the alkylation of isopentane with isobutylene. In addition, there was obtained a large number of fractions boiling below the isononane boiling range and also boiling above the isononane boiling range but below the boiling range of possible polyalkylation products. Consequently, as in the case of the alkylation of isopentane with propylene, the reaction is considerably more complex than it would be on the basis of the direct addition of isobutylene to isopentane.

The investigations of the authors of this article showed that monofluorophosphoric and difluorophosphoric acids saturated with boron trifluoride are the most active of the catalysts studied for the alkylation of isoparaffinic and aromatic hydrocarbons with olefins.

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TAUTOMERISM OF ACYLATED HETEROCYCLIC AMINES AND ITS STUDY BY MEANS OF SPECTRA

Yu. N. Sheinker

(Presented by Academician I. L. Knunyants, December 4, 1956)

In work carried out previously [1-4], it was shown with the aid of spectra that α- and γ-amino derivatives of the N-heteroaromatic series exist in the amino form, and not as imino compounds.

An explanation of this fact can be obtained by application of the law of acid-base equilibrium to the amine-imine tautomeric equilibrium. According to this, the existence of heterocyclic amines in the amino form is considered as a consequence of the considerably higher basicity of the extra-ring imino nitrogen atom in comparison with the basicity of the ring nitrogen, which causes a strong (practically complete) displacement of the equilibrium in the direction of the amino tautomeric form [4].

From these concepts it follows that it is possible for a change in the ratios of the basicities of the two nitrogen atoms responsible for the tautomerism – the ring and the extra-ring nitrogens – to have an effect on the amine-imine tautomeric equilibrium. It would be expected that such a change could be realized by replacement of one of the hydrogen atoms of the amino group by electronegative groups such as acid radicals, which could significantly lower the basicity of, primarily, the extra-ring nitrogen directly bonded to it.

In work devoted to this aim, the acid radicals of acetic and benzoic acids, mono-, di-, and trichloroacetic acids, trifluoroacetic acid, benzenesulfonic and sulfanilic acids, and nitric acid were used. Upon their introduction into the amino group of 2-amino-pyridine and 2-aminothiazole, these radicals formed the corresponding amides.

By a study of the infrared and ultraviolet spectra of the indicated compounds it was shown that depending on the "acidifying" (acidizing) power of the acid radicals (the value of this power can be measured by the strengths of the corresponding acids), the heterocyclic amides exist, indeed, not only in the amino form, but also in the imino form or in a mixture of the two tautomeric isomers. These data were obtained by a comparison of the spectra of the amides with the spectra of their methyl derivatives, which have a fixed amino or imino structure, and also by a consideration of the individual characteristic bands in the infrared spectra.

Thus, the infrared spectra (in the crystalline state) of acetylamino- and benzoylaminopyridine, and also those of the mono- di- and trichloroacetylaminopyridines, had a band characteristic of the amide carbonyl group at 1686-1718 cm^{-1} (at the higher frequencies in the case of the chloroacetyl amides owing to the inductive effect of the electronegative chlorine atoms).

In contrast to the analogous pyridine derivative, the spectrum of 2-trichloroacetylaminothiazole had the carbonyl band at only 1616 cm^{-1}, indicating the imino structure of this compound in the solid state. Indeed, for model compounds with a fixed imino structure (N-methyl-2-acetylpyridonimine, N-methyltrichloroacetylpyridonimine, N-methyl-2-trichloroacetyliminothiazoline) the carbonyl band is observed in the region of 1605-1630 cm^{-1}, being substantially shifted to the region of lower frequency owing to conjugation.

The effect of the stronger acidizing radical of trichloroacetic acid is such that not only 2-trifluoroacetylaminothiazole, but also 2-trifluoroacetylaminopyridine exists in the imino form in the crystalline state (carbonyl band at 1630-1640 cm^{-1}, see Figure 1).

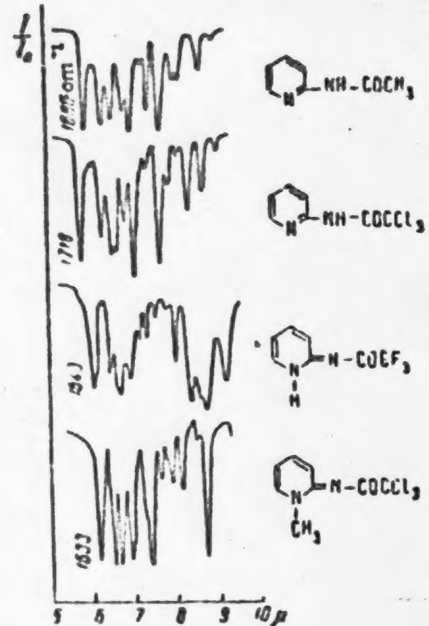


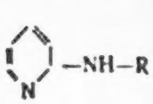
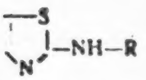
Fig. 1. Infrared absorption spectra of some 2-acylaminopyridines and N-methyl-2-trichloroacetylpyridominine.

In solutions in various solvents, such compounds as 2-acetyl-, 2-monochloroacetyl-, and 2-dichloroacetylaminopyridine have an amino structure (absorption bands in the ultraviolet at 235 and 278 mμ, as in substances with a fixed amino structure). Trichloroacetylaminopyridine, which exists in heptane solution as an amide, exists in alcoholic and, particularly, in aqueous solutions to an appreciable extent as the imide tautomeric form as well as the amide (absorption band at 315-325 mμ, as in N-methyl-2-trichloroacetyl- or N-methyl-2-acetylpyridonimines). In alcoholic and aqueous solutions, 2-trichloroacetylaminothiazole exists practically completely in the imine tautomeric form (ultraviolet band at 305 mμ), and appears as the amide only in heptane solution; alcoholic and aqueous solutions of 2-dichloroacetylaminothiazole contain rather large amounts of the amino form. In the crystalline state, dichloroacetylaminothiazole exists as an amide (infrared carbonyl band at 1702 cm^{-1}.

The infrared spectra of the sulfonamidopyridine and the sulfanilamidopyridine had bands characteristic of the imino grouping N − C = N − SO$_2$ − (940 cm^{-1}), and did not exhibit the band characteristic of the amino configuration N = C − N − SO$_2$ − (1040 cm^{-1} and 850-860 cm^{-1}). In the ultraviolet region, aqueous solutions of these compounds absorbed analogously to model compounds of fixed imino form; a small content of the amino forms appeared in alcoholic solutions, and they predominated in dioxane-heptane solutions (Figure 2). In contrast to the pyridine derivatives,

TABLE 1

Content of Amino Form (%)

Structural formula	R	n-Heptane solution	Dioxane solution	Alcohol solution	Aqueous solution
	COCH$_3$	∼100	∼100	∼100	∼100
	COCHCl$_2$	∼100	∼100	99.9	99.0
	COCCl$_3$	∼100	99.8	99.0	93.7
	SO$_2$C$_6$H$_4$NH$_2$	—	99.1	78.0	18.5
	SO$_2$C$_6$H$_5$	99	95.5	45	11
	NO$_2$	—	87.4	17	∼0
	COCH$_3$	∼100	∼100	∼100*	∼100
	COCHCl$_2$	∼100	99.6	90	45
	COCCl$_3$	93	60	3.5	∼0
	SO$_2$C$_6$H$_4$NH$_2$	∼0	∼0	∼0	∼0
	SO$_2$C$_6$H$_5$	∼0	∼0	∼0	∼0
	NO$_2$	∼0	∼0	∼0	∼0

---

* The previously noted [5] presence of several per cent of the imine tautomeric form in an alcoholic solution of 2-acetylaminothiazole was not confirmed by repeated measurements.

2-sulfamidothiazole* retained the imino structure both in the crystalline state and in all solvents.

2-Nitraminothiazole behaved similarly, while for 2-nitraminopyridine, which had an imino structure in the crystalline state and in aqueous and alcoholic solutions (infrared bands at 1615 cm^{-1} and 1543 cm^{-1} and ultraviolet bands at 273 mμ and 320 mμ), an appreciable content of the aminotautomeric form was observed in dioxane solution.

Thus, by using radicals differing in acidizing power, it would be possible to affect the position of the tautomeric equilibrium, obtaining derivatives having one or the other tautomeric structure.

The quantitative data on the equilibrium content of amino and imino tautomeric forms of the compounds studied in various solvents, which were obtained from ultraviolet spectra, are presented in Table 1.

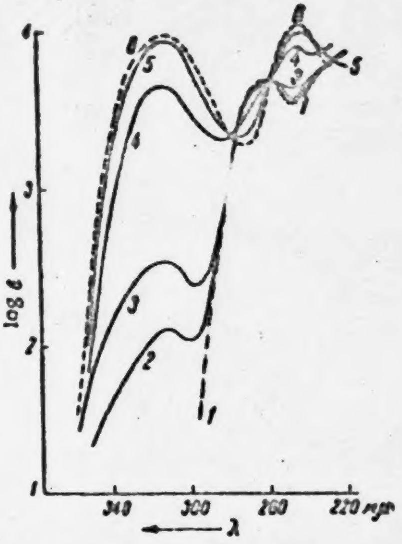


Fig. 2. Ultraviolet absorption spectra. 1) 2-methylsulfonamidopyridine in alcohol, 2) 2-sulfonamidopyridine in n-heptane, 3) same in dioxane, 4) same in alcohol, 5) same in water, 6) N-methyl-2-sulfonpyridonimine in alcohol.

From these data it follows that shifting of the tautomeric equilibrium in the direction of the imino form requires acyl groups of high acidizing power, the minimum value of this acidizing power differing for the different heterocyclic amines. Conversion to the imino form proceeds more easily for derivatives of 2-aminothiazole than for derivatives of 2-aminopyridine.

The solvents can be arranged in the following series with respect to their ability to shift the amine-imine equilibrium, each succeeding member of the series possessing increased ability to shift the equilibrium in the direction of the imine tautomeric form: heptane, dioxane, alcohol, water. In the crystalline state, the substances exist in only one tautomeric form – the amine form for compounds with acyl radicals of comparatively low or average acidizing power, and the imine form for compounds with radicals of high acidizing power.

In our opinion, all of these data confirm the correctness of the approach to amine-imine (and, in general, protolytic) tautomeric equilibria as equilibria having an acid-base nature.

This conclusion is also confirmed by the following quantitative comparisons. If the negative logarithms of the tautomeric equilibrium constants, pK_s, for the compounds investigated are plotted graphically, plotting the values for one solvent along one axis and the values for a different solvent along the other axis, the points fall on a straight line with a slope of 45° to the abscissa (Figure 3), and the line, therefore, fits the equation $pK_{s_1} = pK_{s_2} + \text{const.}$

As was first pointed out by M. I. Kabachnik [6] with reference to keto-enol equilibrium, the existence of such a relationship between tautomeric equilibrium constants in two solvents indicates compliance of the tautomeric system investigated with the Bronsted-Izmailov rule [7] and, consequently, with the relationships determining acid-base equilibria.

Considering that the constant term in the above equation of the straight line is equal to $\frac{\Delta F_{s_2} - \Delta F_{s_1}}{2.3 RT}$, where $\Delta F_{s_2} - \Delta F_{s_1}$ is the free energy change of the tautomeric system during the change from one solvent to another, this latter value is easily calculated, since we have from the graph the value of the constant for the entire series of compounds investigated (for a given pair of solvents). The values of $\Delta F_{s_2} - \Delta F_{s_1}$ calculated from the experimental data are 2.1 kcal/mole for the change from dioxane to alcohol and 1.2 kcal/mole for the change from alcohol to water.

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* The investigation of the sulfamides of the thiazole series was carried out jointly with I. Ya. Postovsky and V. V. Kushkin; the results of this work will be reported in detail in the future.

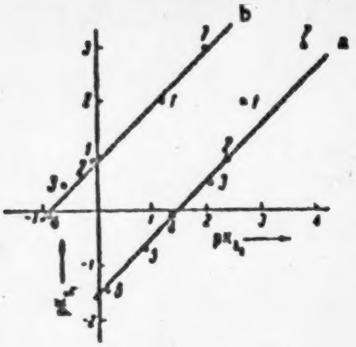

Fig. 3. Relation between pK_a in two solvents: s_1 – ethyl alcohol; s_2 – dioxane (a) and water (b). 1) 2-trichloroacetylaminopyridine, 2) 2-dichloroacetylaminothiazole, 3) 2-sulfanilamidopyridine, 4) 2-sulfonamidopyridine, 5) 2-nitraminopyridine, 6) 2-trichloracetylaminothiazole, 7) 2-dichloroacetylaminopyride.

EXPERIMENTAL

The infrared absorption spectra were taken with an IKS-11 infrared spectrometer, and the ultraviolet spectra with an SF-4 spectrophotometer. The acylated heterocyclic amines were prepared by reaction of the chlorides of the corresponding acids with 2-aminopyridine and 2-aminothiazole in pyridine or benzene medium. In this manner were prepared: 2-chloroacetylaminopyridine, m.p. <110° (decomp.), found Cl 20.8%, calculated Cl 20.8%; 2-dichloroacetylaminopyridine, m.p. 69-70.5°, found Cl 34.5%, calculated Cl 34.6%; 2-dichloroacetylaminothiazole, m.p. 180-180.5°, found Cl 33.9%, calculated Cl 33.6%; 2-trichloroacetylaminopyridine, m.p. 84-85°, found Cl 44.4%, calculated Cl 44.5%; 2-trichloroacetylaminothiazole, m.p. 194-195°, found Cl 43.5%, calculated Cl 43.4%; 2-sulfonamidopyridine, m.p. 171°; 2-sulfonamidothiazole, m.p. 170°. By the reaction of the amide with the corresponding acid anhydride were prepared 2-trifluoroacetylaminopyridine, m.p. 98-101°, found: C 44.0%, H 2.49%, calculated: C 44.2%, H 2.63%; 2-trifluoroacetylaminothiazole, m.p. 156-157°, found: C 30.32%, H 1.59%, calculated: C 30.60%, H 1.53%; 2-acetylaminopyridine, m.p. 71°. By nitration of the corresponding amines with concentrated nitric acid by the method of Chichibabin and Razorenov [8] were synthesized 2-nitraminopyridine, m.p. 184°, and 2-nitraminothiazole, m.p. <180° (decomp.).

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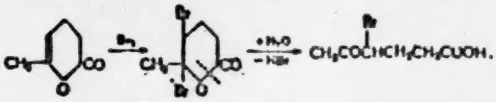
δ-LACTONES. PREPARATION OF ACYLATED BUTYROLACTONES FROM γ-BROMO-δ-KETO ACIDS

N. P. Shusherina, M. Yu. Lurye and R. Ya. Levina

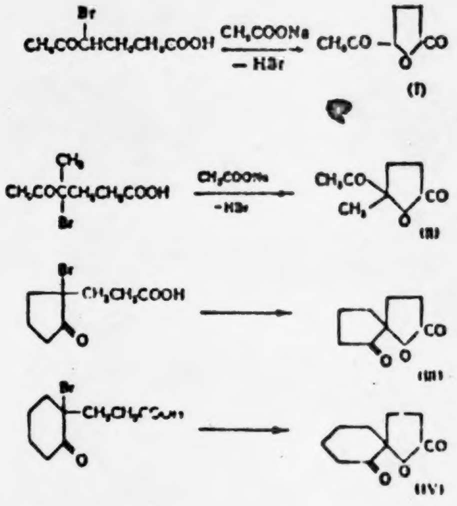
(Presented by Academician A. N. Nesmeyanov, December, 1956)

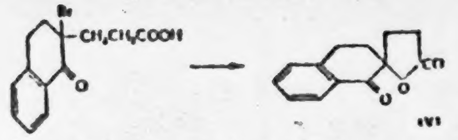
In our previous communications [1, 2], we described a method for the preparation of γ-bromo-δ-keto acids by the reaction of dibromides of unsaturated δ-lactones with water; for example [2]:


Br₂
Br
Br
+H₂O
−HBr
CH₃COCHCH₂CH₂COOH.

In the present work, it was shown that the γ-bromo-δ-keto acids prepared by such a method are converted by the action of a saturated aqueous solution of sodium acetate in the cold to butyrolactones acylated in the δ-position.

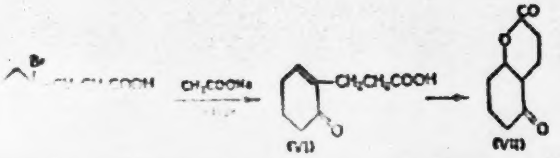
Using this reaction, we prepared, in good yields, from the corresponding γ-bromo-δ-keto acids δ-acetylbutyrolactone [(I), yield 60.5%], δ-acetyl-δ-methylbutyrolactone [(II), 49.2%], the lactone of 2-hydroxy-2-(β-carboxyethyl)cyclopentanone [(III), 61.5%], the lactone of 2-hydroxy-2-(β-carboxyethyl) cyclohexanone [(IV), 56%], and the lactone of 2-hydroxy-2-(β-carboxyethyl)-1-tetralone [(V), 71%]:


CH₃COCHCH₂CH₂COOH
Br
CH₃COONa
− HBr
CH₃CO
CO
(I)
CH₃
CH₃COCCH₂CH₂COOH
Br
CH₃COONa
−HBr
CH₃CO
CH₃
CO
(II)
Br
CH₂CH₂COOH
O
CO
(III)
Br
CH₂CH₂COOH
O
CO
(IV)



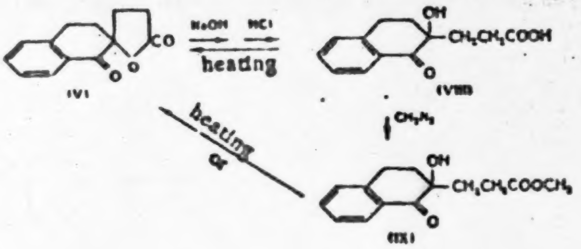
Thus, this reaction can serve as a method for the preparation of acylated butyrolactones.

In all cases except the first, it might be assumed that, in addition to the butyrolactones, the isomeric six-membered lactones (VII) would be formed if the reaction proceeds through the intermediate formation of unsaturated keto acids (VI), for example:



However, this assumption fails, since it was shown by experiment that a specially synthesized unsaturated keto acid VI is not changed by the action of a saturated aqueous solution of sodium acetate. Substances I – V were not titratable by aqueous or alcoholic solutions of alkali, did not decolorize bromine water, and gave semicarbazones (except V).

The presence of a lactone ring in the prepared compounds was confirmed by conversion of one of them (V) to the corresponding γ-hydroxy acid. By heating lactone V with an aqueous solution of sodium hydroxide and subsequent acidification, we were able to obtain the hydroxy acid (VIII), and from it, by the action of azomethane, we obtained the methyl ester (IX); the hydroxy acid VIII was readily converted to the lactone V by heating, and the methyl ester of the hydroxy acid, IX, was converted to the lactone V by heating or by the action of HBr in the cold.



This reaction and also the analytical data confirm the structure of substances I – V as acylated butyrolactones.

EXPERIMENTAL

5-Acetylbutyrolactone (I). 10 g of crystalline γ-bromo-γ-acetylbutyric acid (m.p. 39-41° [2]), 19.5 g of sodium acetate, and 20 ml of water were stirred in the cold for 2 hours; the reaction mixture was then extracted with ether (in an extractor) for 10 hours. The 5-acetylbutyrolactone (3.7 g, 60.5% yield) had the following constants: b.p. 143-144° at 15-17 mm, n_D^{20} 1.4630, d^{20} 1.1990, MR_D 29.41. Calculated for $C_6H_8O_3$, MR_D 29.37.

Found %: C 56.20, 55.75; H 6.67, 6.37. $C_6H_8O_3$. Calculated %: C 56.26; H 6.30.

Semicarbazone m.p. 180-181° (from alcohol).

Found %: N 22.69, 22.63. $C_7H_{11}O_3N_3$. Calculated %: N 22.69.

Literature data [3]: b.p. 113-116° at 10 mm, n_D^{20} 1.4657, d_4^{20} 1.222, MR_D 28.76, Semicarbazone m.p. 184-185°.

5-Methyl-5-acetylbutyrolactone (II) was prepared by the same route from γ-bromo-γ-acetylvaleric acid (m.p. 79-80° [1]) in 43.2% yield: b.p. 119° at 13 mm, n_D^{20} 1.4600, d_4^{20} 1.1340, MR_D 34.34. Calculated for $C_7H_{10}O_3$ MR_D 33.99.

Found %: C 59.19, 59.37; H 7.18, 7.34. $C_7H_{10}O_3$. Calculated %: C 59.17; H 7.08.

Semicarbazone m.p. 180.5° (from alcohol).

Found %: N 21.10, 20.88. $C_8H_{13}O_3N_3$. Calculated %: N 21.09.

Literature data [4] (prepared by hydration of γ-ethynyl-γ-valerolactone): b.p. 115-116° at 10 mm; semicarbazone m.p. 182-183°.

Lactone of 2-hydroxy-2-(β-carboxyethyl)cyclopentanone (III). 4 g of 2-bromo-2-(β-carboxyethyl) cyclopentanone (m.p. 55-56° [2]), 7 g of sodium acetate, and 8 ml of water were vigorously stirred for two hours; the resulting crystals of ketolactone (III) were filtered, washed with water, and dried (1.6 g; 61.5% yield): m.p. 105-106° (from ether).

Found %: C 62.35, 62.23; H 6.50, 6.44. $C_8H_{10}O_3$. Calculated %: C 62.36; H 6.54.

Semicarbazone m.p. 230° (with decomposition, from alcohol).

Found %: N 19.99, 19.57. $C_9H_{13}O_3N_3$. Calculated %: N 19.89.

The lactone of 2-hydroxy-2-(β-carboxyethyl)cyclohexanone (IV) was obtained in 56% yield by the same method as lactone (III) from 2-bromo-2-(β-carboxyethyl)cyclohexanone (m.p. 70-71°): b.p. 148-149° at 7 mm, m.p. 54-55° (from ether).

Found %: C 64.36, 64.34; H 7.38, 7.34. $C_9H_{12}O_3$. Calculated %: C 64.26; H 7.14.

Semicarbazone m.p. 200° (from alcohol, with decomposition).

Found %: N 18.67, 18.85 $C_{10}H_{15}O_3N_3$. Calculated %: N 18.66.

Literature data [5] (prepared, together with other reaction products, by the oxidation of o-methylenecyclohexanone dimer with subsequent treatment with alkali): m.p. 60°, semicarbazone m.p. 196° (with decomposition).

Lactone of 2-hydroxy-3-(β-carboxyethyl)-1-tetralone (V). 6 g of 2-bromo-2-(β-carboxyethyl)-1-tetralone (m.p. 143°), 12 g of sodium acetate, 15 ml of water, and 3 ml of alcohol were stirred for an hour and left overnight. After evaporation of the alcohol, the crystals, which had precipitated from the solution on standing, were washed with water and dried. The resulting ketolactone V melted at 100-101° (from gasoline).

Found %: C 72.54, 72.65; H 5.74, 5.75. $C_{13}H_{12}O_3$. Calculated %: C 72.22; H 5.55.

We were unable to prepare the semicarbazone of ketolactone V under the usual conditions.

2-Hydroxy-2-(β-carboxyethyl)-1-tetralone (VIII). 4 g of ketolactone V was dissolved in 10 ml of a 10% aqueous solution of sodium hydroxide with mild heating. Concentrated hydrochloric acid was added dropwise, with cooling, to this solution. The precipitated hydroxyketo acid VIII (3.9 g), after washing with distilled water and drying in a vacuum desiccator, melted at 116-117° (the melting point was determined in an apparatus preliminarily heated to 110°.

Found %: C 72.54, 72.65; H 5.74, 5.75. $C_{13}H_{12}O_3$. Calculated %: 72.22; H 5.55.

During crystallization from alcohol, hydroxy acid VIII was partially converted, and completely converted on heating, to the original ketolactone V (m.p. 100°)

2-Hydroxy-2-(β-carbomethoxyethyl)-1-tetralone (IX). To 3.8 g (0.017 mole) of hydroxy acid VIII was added 36 ml of an ethereal solution containing ~0.03 mole of diazomethane. After completion of the reaction, the ether was evaporated under vacuum, and the remaining oil crystallized on long standing: m.p. 62-62.5°. During an attempt to recrystallize this hydroxy acid ester from alcohol, and also during distillation or on treatment with concentrated hydrobromic acid in the cold, ketobutyrolactone V (m.p. 100°) was formed in quantitative yield.

Attempt at the lactonization of the unsaturated keto acid (VI). Unsaturated keto acid (VI)* (m.p. 75-76°; semicarbazone m.p. 180-181°) was treated with an aqueous solution of sodium acetate under the same conditions as the 2-bromo-2-(β-carboxyethyl)cyclohexanone. The original acid, VI, with m.p. of 75°, was recovered from the reaction mixture. Semicarbazone m.p. 180°; a mixture of this semicarbazone with that of the original unsaturated keto acid melted without depression of the melting point.

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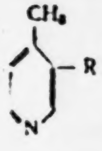
* The synthesis and transformations of this unsaturated δ-keto acid will be described in a subsequent communication.

CERTAIN CHEMICAL PECULIARITIES OF 2,6-DICHLORO DERIVATIVES OF PYRIDINE

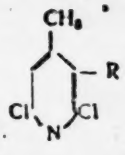
L. N. Yakhontov

(Presented by Academician I. N. Nazarov, December 17, 1956)

In the course of the synthesis of derivatives of quinuclidine, a series of 3,4-disubstituted pyridines (I) and their 2,6-dichloro derivatives (II) have been obtained [1, 2]:



I



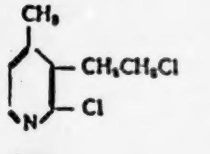
II

R = $-C_2H_5$; $-CH=CH_2$; $-CH_2-CH_2Cl$; $-CH_2CH_2OH$; $-CH_2CH_2OCH_3$; $-CH_2CH_2OOCCH_3$; $-COOH$; $-COOC_2H_5$; $-COCH_3$.

A comparison of the properties of these compounds exposed certain chemical peculiarities of the 2,6-dichloro derivatives of pyridine; II, which are connected with the α, α′-halogen atoms. II, in contrast to the corresponding dehalogenated compounds, I, do not form salts with mineral acids, and do not form picrates.

These data are in agreement with the absence from the literature of reports of hydrochlorides or picrates of any 2,6-dihalo derivatives of pyridine and with the statement of Sell and Dootson [3] that 2,6-dichloropyridine does not form a chloroplatinate nor a complex salt with mercuric chloride.

It should be noted that elimination of only one α-chloro substituent leads to a compound which forms a hydrochloride. We synthesized 2-chloro-4-methyl-3-(β-chloroethyl)-pyridine [2], and prepared its hydrochloride (III) by treatment of an ethereal solution of the base with an alcoholic solution of hydrogen chloride.



HCl

III

The hydrochloride is stable in air, but is readily hydrolyzed by water.

Another peculiarity of 2,6-dichloro derivatives of pyridine is that they do not form quaternary salts on refluxing for many hours in acetone solution with methyl iodide. At the same time, the corresponding dehalogenated compound, I, readily forms the methiodide with methyl iodide in acetone at room temperature. These data are in agreement with the report of Wibaut [4], who was able to prepare the methiodide of 2,6-dibromopyridine in very small yield only by carrying out the reaction in a tube at 100° for 6 hours.

A third peculiarity of 2,6-dichloro derivatives of pyridine, II, is their inability to form N-oxides, which in the case of the dehalogenated compounds, I, are readily prepared by heating with hydrogen peroxide in glacial acetic acid.

The difficulty in the formation of salts, quaternary salts, N-oxides, and complex compounds at the nitrogen atom of 2,6-dichloro derivatives of pyridine could be due both to steric hindrance and to suppression of the basic properties of the nitrogen by a decrease in the electron density at the nitrogen atom owing to the α, α' -halogen atoms, which are electron acceptors. In support of the latter factor is also the lack of reactivity of the methyl group in the 4-position of 2,6-dichloro derivatives of pyridine, II.

Examples. A. II, in contrast to I, do not enter into condensation reactions with carbonyl compounds (aldehydes, mesoxalic ester).

B. II is unchanged on heating with selenium dioxide under various conditions, while the γ -methyl group of I is readily oxidized by selenium dioxide. For example, 3-(β -acetoxyethyl)-4-methylpyridine, on heating with selenium dioxide in boiling toluene for 25 minutes, forms 3-(β -acetoxyethyl)-isonicotinic acid. M.p. 155-156° (from toluene).

Found %: C 57.13, 57.29; H 5.61; 5.64; N 6.30. $C_{10}H_{11}O_4N$. Calculated %: C 57.41; H 5.26; N 6.69

2,6-Dichloro-3-(β -acetoxyethyl)-4-methylpyridine (II, R = $-CH_2CH_2$-$OOCCH_3$) is quantitatively recovered unchanged after heating with selenium dioxide in boiling toluene for 3 hours, and also after heating without a solvent for $^1/_2$ hour at 160-165° or at 250° for 10 minutes.

N. A. Preobrazhensky and A. A. Baer [5] indicated that on heating 4-methylnicotinic acid with an excess of thionyl chloride, in addition to the formation of the acid chloride, there was substitution of hydrogen atoms in the γ -methyl group by chlorine atoms. Saponification of the resulting acid chloride of 4-trichloromethylnicotinic acid led to cinchomeronic acid.

It would be expected that in the corresponding 2,6-dichloro-4-methylnicotinic acid the hydrogen atoms in the γ -methyl group would be less active.

Actually, on heating our preparation of 2,6-dichloro-4-methylnicotinic acid (II, R = $-COOH$) with an excess of thionyl chloride under the same conditions, we obtained only the acid chloride of 2,6-dichloro-4-methylnicotinic acid, which, on heating with absolute alcohol, was converted into the ethyl ester of 2,6-dichloro-4-methylnicotinic acid with a yield of 91% of the original acid.

Finally, it should be noted that, according to literature data [6], the Rosenmund reaction is applicable only to the acid chloride of 2,6- (or 2,4-) dichloropyridinecarboxylic acid. The corresponding dehalogenated acids of the pyridine series are not converted to aldehydes by this route.

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THE STRONG TRANS EFFECT OF THE HYDROXO GROUP IN THE DIOXIMINES OF TRIVALENT COBALT

A. V. Ablov and N. M. Samus

(Presented by Academician I. I. Chernyaev, December 25, 1956)

In studying the acid properties of nitro-bis-dimethylglyoximoaquocobalt $[CoH_2O(DH)_2NO_2]$ it was found that this compound is completely soluble in concentrated alkali, forming a dark-red solution. The slight heating of this solution gives a copious red-brown crystalline precipitate having the composition $K[Co(DH)_2(OH)_2]\cdot 3H_2O$.* The sodium salt was also obtained in the same manner.

The reaction of nitric acid with these salts yields the red bis-dimethylgyoximodiaquocobalt nitrate, in which connection the formation of an intermediate product is quite distinct:

$$K[Co(DH)_2(OH)_2] + HNO_3 = [CoH_2O(DH)_2OH] + KNO_3;$$
$$[CoH_2O(DH)_2(OH)] + HNO_3 = [Co(H_2O)_2(DH)_2]NO_3.$$

Carefully reacting a solution of potassium carbonate with chloro-bis-dimethylglyoximoaquocobalt, we were unable to obtain the intermediate compound—hydroxo-bis-dimethylglyoximoaquocobalt—in a pure state. If the chloroaquo compound is covered with alkali, then the dihydroxo compound is obtained. This method is the more convenient for obtaining the latter.

Below we give the conductivity and pH values for three of the above described compounds at a solution dilution of 1000 liter/mole:

	μ_{1000}^{25}, ohm^{-1}cm^{2}	pH
$K[Co(DH)_2(OH)_2]\cdot 3H_2O$	132.8	9.49
$[CoH_2O(DH)_2(OH)]\cdot H_2O$	9.7	7.02
$[Co(H_2O)_2(DH)_2]NO_3$	217.9	5.79

Potassium dihydroxo-bis-dimethylglyoximocobaltate (III) gives an alkaline reaction due to hydrolysis in accord with the equation:

$$[Co(DH)_2(OH)_2]^- + H_2O \rightleftarrows [CoH_2O(DH)_2(OH)] + OH^-$$

The diaquo-bis-dimethylglyoximocobalt (III) ion dissociates in accord with the equation:

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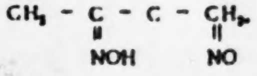
* DH designates the dimethylglyoxime moiety 

$$CH_3-\underset{NOH}{\underset{\|}{C}}-\underset{NO}{\underset{\|}{C}}-CH_3.$$

$$[\mathrm{Co(H_2O)_2(DH)_2}]^+ \rightleftarrows [\mathrm{CoH_2O(DH)_2(OH)}] + \mathrm{OH^+}.$$

Hydroxo-bis-dimethylglyoximoaquocobalt (III) is an ampholyte:

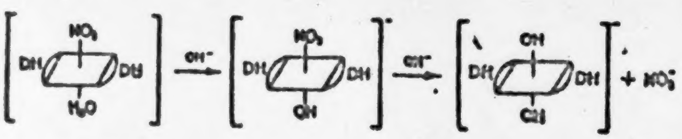
$$[\mathrm{CoH_2O(DH)_2(OH)}] \rightleftarrows [\mathrm{Co(DH)_2(OH)_2}]^- + \mathrm{H^+}.$$
$$[\mathrm{CoH_2O(BH)_2(OH)}] + \mathrm{H^+} \rightleftarrows [\mathrm{Co(H_2O)_2(DH)_2}]^+.$$

The heating of the dihydroxo-bis-dimethylglyoximocobaltate (III) with concentrated hydrochloric acid gives the dichloro-bis-dimethylglyoximocobaltic acid $H[Co(DH)Cl]$ of characteristic green color. This reaction causes assigning the same configuration to all of the cobalt dioximines of the $[Co(DH)_2X_2]$ type.

Using the rules of the trans effect as a basis, one of us expressed the theory that in compounds of the $[Co(DH)_2X_2]$ type the two X radicals are found in the trans position to each other [1]. Further studies confirmed this spatial configuration of the trivalent cobalt dioximines [2,3]. Recently, on the basis of studying the infrared spectra, Nakahara [4] also obtained proof of the transconfiguration

$$\mathrm{H[Co(DH)_2Cl_2]}.$$

Proceeding from the rules of the trans effect as postulated by I. I. Chernyaev [5], the transition of nitro-bis-dimethylglyoximoaquocobalt into potassium dihydroxo-bis-dimethylglyoximocobaltate (III) can be explained in the following manner. When reacted with alkali the nitroaquo compound migrates first into the nitrohydroxo-bis-dimethylglyoximocobaltate (III) $K[Co(DH)_2(OH)NO_2]\cdot H_2O$. The hydroxo group, which should be assigned a stronger trans effect than for the nitro group, weakens the bond between the NO_2 group and the cobalt atom, and the NO_2 group is replaced by the hydroxo group:



The intermediate product $K[Co(DH)_2(OH)NO_2]\cdot H_2O$ was obtained by the action of potassium carbonate on the nitroaquo compound.

The theory that in trivalent cobalt dioximines the hydroxo group shows a strong trans effect was evolved to explain the action of alkali on the anion of di-isothiocyano-bis-dimethylglyoximocobaltic acid [2], but at the time lacked sufficient basis. By treating isothiocyano-bis-dimethylglyoximoaquocobalt with alkali, we were now able to isolate the dihydroxo-bis-dimethylglyoximocobaltate (III) in crystalline form.

As a result, the hydroxo group shows a greater trans activity than either the thiocyano or nitro group. Considering that the thiocyano group shows a greater trans activity than does the nitro group [3], these three groups should be arranged in the following order of increasing trans activity in the dioximines of trivalent cobalt:

$$\mathrm{OH > NCS > NO_2}$$

EXPERIMENTAL

Action of alkalies on nitro-bis-dimethylglyoximoaquocobalt. a) Two grams of nitro-bis-dimethylglyoximoaquocobalt [6] was covered with 10 ml of 50% potassium hydroxide solution. On stirring, a dark-red solution was formed. Heating of the latter gave a copious crystalline precipitate. The obtained salt was transferred to a glass filter, washed with either absolute alcohol or butanol, and at the end with ether. The filtrate, after some standing, deposited a new portion of the product. The total yield was 75% of theory. Under the microscope the substance appeared as dark-red slender quadrangular prisms. Extremely soluble in water, and insoluble in absolute alcohol and ether.

A solution of the potassium salt of the dihydroxo acid forms precipitates with $Rb^{\cdot}$, Cs, $Hg_2^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$. For analysis the substance was dried between filter paper. The loss in weight at 105° was 13.50%.

Found %: Co 14.08, 14.07; N 13.64, 13.31. $K[Co(C_4H_7N_2O_2)_2(OH)_2]\cdot 3H_2O$. Calculated %: Co 14.17; N 13.46; H_2O 13.00.

The potassium salt of dihydroxo-bis-dimethylglyoximocobaltic acid was first obtained by Cambi [7] by treating a suspension of $[CoDH_2(DH)Br_2]$ in absolute alcohol with 3 moles of potassium alcoholate.

b) The action of sodium hydroxide on the nitroaquo compound gave sodium dihydroxo-bis-dimethylglyoximocobaltate (III) $Na[Co(DH)_2(OH)_2]\cdot 5H_2O$, which was obtained as a brown-red crystalline precipitate. Under the microscope it appeared as elongated quadrangular plates. The yield was 65% of theory. The loss in weight at 105° was 20.02%.

Found %: Co 13.39, 13.21; N 12.82. $Na[Co(DH)_2(OH)_2]\cdot 5H_2O$. Calculated %: Co 13.51; N 12.84; H_2O 20.65.

The substance, after drying at 105°, avidly absorbed moisture from the air.

Diaquo-bis-dimethylglyoximocobalt (III) nitrate $[Co(H_2O)_2(DH)_2]NO_3$. The salt of the dihydroxo acid was dissolved in the minimum amount of cold water. Concentrated nitric acid was added in drops to this until a precipitate began to form. With cooling the amount of the latter increased. The substance was transferred to a glass filter, washed with absolute alcohol, and then with ether. Extremely soluble in water. Yield 50% of theory.

Found %: Co 14.94, 15.06; N 18.06. $[Co(H_2O)_2(DH)_2]NO_3$. Calculated %: Co 15.23; N 18.03.

The gentle heating of the diaquo nitrate with excess potassium thiocyanate, followed by acidification of the solution, gave diisothiocyano-bis-dimethylglyoximocobaltic acid in nearly quantitative yield. Heating with hydrogen halide acids leads to green dihalo acids, for example $H[Co(DH)_2Cl_2]$.

Hydroxo-bis-dimethylglyoximoaquocobalt $[CoH_2O\cdot(DH)_2OH]\cdot H_2O$. Chloro-bis-dimethylglyoximoaquocobalt [8] was covered with a cold concentrated solution of either potash or soda and the mixture stirred until the color changed completely from a grayish-green to a light-yellow. The substance was filtered through a glass filter, washed with a little cold water, alcohol, and at the end with ether. Yield 65% of theory. Under the microscope the hydroxoaquo compound appeared as stout quadrangular prisms, readily soluble in water and alcohol.

Found %: Co 17.19, 17.28; N 16.58. $[CoH_2O(DH)_2(OH)]\cdot H_2O$. Calculated %: Co 17.22; N 16.38.

Hydroxo-bis-dimethylglyoximoaquocobalt is transformed into the dihydroxo compound when reacted with one equivalent of alkali, and gives the dichloro acid when reacted with concentrated hydrochloric acid.

When treated in the cold with alkali the chloro-bis-dimethylglyoximoaquocobalt yields the dihydroxo compound, which deposits in a crystalline state after some standing. This is a very convenient method for obtaining the compound.

Potassium nitrohydroxo-bis-dimethylglyoximocobaltate (III) $K[Co(DH)_2(OH)\cdot NO_2]\cdot H_2O$. The powdered nitro-bis-dimethylglyoximoaquocobalt was sifted into a concentrated solution of potassium carbonate and the mixture stirred until the brownish-red color of the the solid phase had changed completely to a yellow. The substance was transferred to a filter, rapidly washed with cold water, then with alcohol, and finally with ether. Yield 70% of theory. Under the microscope the potassium nitro-hydroxo-bis-dimethylglyoximocobaltate (III) appeared as a finely crystalline yellow powder.

When treated with water the nitroaquo compound was transformed into nitro-bis-dimethylglyoximoaquocobalt, and when reacted with alkali it gave the dihydroxo compound.

The air-dried substance was taken for analysis. The loss in weight at 105° was 4.83%.

Found %: Co 14.37, 14.46, 14.33; N 17.46. $K[Co(DH)_2(OH)NO_2] \cdot H_2O$. Calculated %: Co 14.40; N 17.11; H_2O 4.39.

Sodium isothiocyanohydroxo-bis-dimethylglyoximocobaltate (III) $Na[Co(DH)_2NCS(OH)] \cdot 3H_2O$. Isothiocyano-bis-dimethylglyoximoaquocobalt was covered at room temperature with 50% sodium hydroxide solution. On stirring, the isothiocyanoaquo compound was completely transformed to a chestnut-red crystalline substance, which was rapidly suction-filtered on a glass filter, washed with absolute alcohol, and then with ether. Under the microscope it appeared as stout quadrangular prisms. Yield 60% of theory.

When treated with water, the isothiocyanohydroxo compound is converted to the yellow finely crystalline isothiocyano-bis-dimethylglyoximoaquocobalt.

When kept in the air for a long time the isothiocyanohydroxo-bis-dimethylglyoximocobalt, under the influence of moisture and carbon dioxide, is also transformed into the isothiocyanoaquo compound.

The substance taken for analysis had been dried between filter paper.

Found %: Co 13.20, 13.30; [illegible], 12.85. $Na[Co(C_4H_7N_2O_2)_2(OH)NCS] \cdot 3H_2O$. Calculated %: Co 13.35; CNS 13.16.

When heated with concentrated sodium hydroxide solution, the isothiocyanohydroxo-bis-dimethylglyoximocobalt yields sodium dihydroxo-bis-dimethylglyoximocobaltate (III).

Found %: Co 13.40; H 12.90. $Na[Co(C_4H_7N_2O_2)_2(OH)_2] \cdot 5H_2O$. Calculated %: Co 13.51; N 12.84.

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STUDY OF THE REACTION OF THE ESTERS OF PHOSPHOROUS ACID WITH ALKYL HALIDES BY PHYSICOCHEMICAL ANALYSIS METHODS

Academician B. A. Arbuzov and A. V. Pushenkova

The mechanism of the A. E. Arbuzov rearrangement has been a topic of study for some 50 years now. A. E. Arbuzov [1] believes that the rearrangement of phosphites into the esters of alkylphosphinic acids is a two-stage process with the formation of a phosphonium type of intermediate product. Such a mechanism was demonstrated by him experimentally for the aromatic phosphites. The opinion exists that for the aliphatic phosphites the intermediate products show immediate spontaneous decomposition and are incapable of existence as such [2]. However, some investigators believe that the rearrangement can proceed by a different mechanism, without the formation of the addition product of the alkyl halide to the phosphite [3,4].

In this communication we discuss the data obtained by us in studying the A. E. Arbuzov rearrangement by physicochemical analysis methods. Our main study problem was to elucidate the possibility of using the composition-property diagram to answer the question of whether an intermediate product is formed in the rearrangement of the aliphatic phosphites to the esters of phosphinic acids.

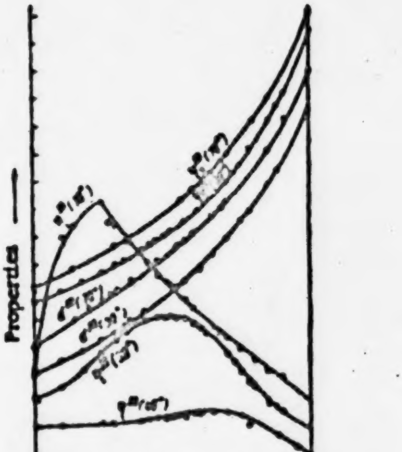

Fig. 1.

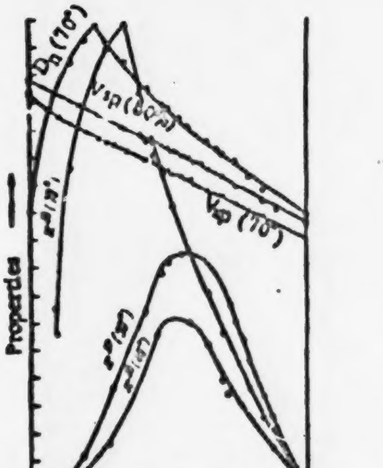

Рис. 2

Fig. 2.

We studied the reaction of triethyl phosphite with ethyl iodide, ethyl bromide and dibromodiethyl ether, and also the reaction of triphenyl phosphite with methyl and ethyl iodide, at various temperatures. The constants were measured at 20° after previous heating of the mixtures in thermostats at given temperatures. A temperature of 20° was chosen for the measurements because of the volatility of one of the components.

In Figs. 1 and 2 we have plotted on the composition-property diagram the measured values of the constants for the triethyl phosphite-ethyl iodide system at various temperatures.

The curves for the index of refraction and the density are convex to the composition axis, and consequently do not reflect chemical reaction.

The isotherms of the specific electroconductivity κ, of the natural compression $D_{natural}$, and especially of the viscosity η, suggest interaction of the components. A shift of the maximum to the left with elevation of the temperature is characteristic for the isotherms of η, $D_{natural}$ and κ.

The enumerated isotherms, reflecting chemical reaction between the components, do not make it possible to decide whether an intermediate product is formed or whether it is absent. Evidently, the composition of the system is a complex one, and the intermediate product, in the case of its formation, partially decomposes into alkyl halide and the ester of the phosphinic acid.

The results of studying the system triethyl phosphite-α,β-dibromodiethyl ether represent considerable interest. According to the data of V. S. Abramov [5], for this system the reaction of the components begins even at room temperature and leads to the formation of the intermediate product of the A. E. Arbuzov rearrangement.

As follows from Figs. 3 and 4, the isotherms of n_D^{20} and d^{20}, the same as in the case of ethyl iodide, are convex to the co[illegible] the deviation from additivity is considerably less, especially for the density isotherm, the co[illegible] extremely slight.

The deviations of the specific volume isotherm $\Delta v_{specific}$ and of the natural compression isotherm $D_{natural}$, calculated in accord with Byron, distinctly suggest that the maximum compression is obtained is characterized by a peculiar shape. Its S-shape with the presence of a singular inflection point at a 1:1 ratio of the components suggests not only interaction of the components, but also association of one of the components, evidently of the α,β-dibromodiethyl ether.

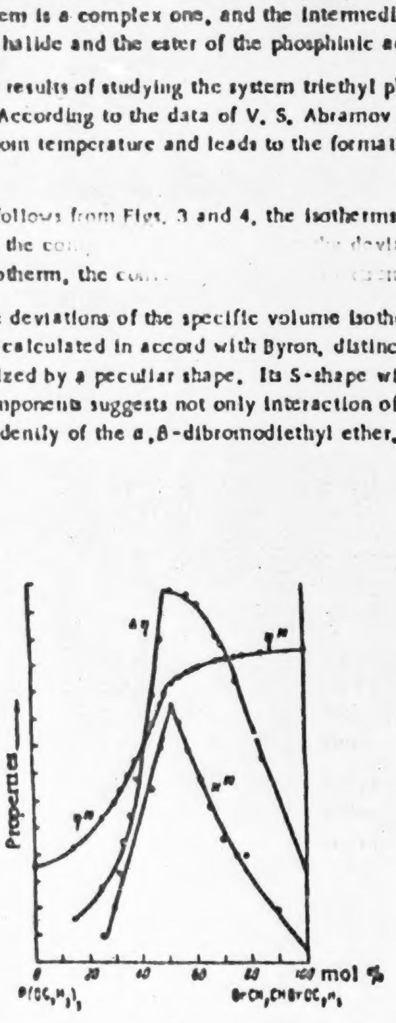

Fig. 3.

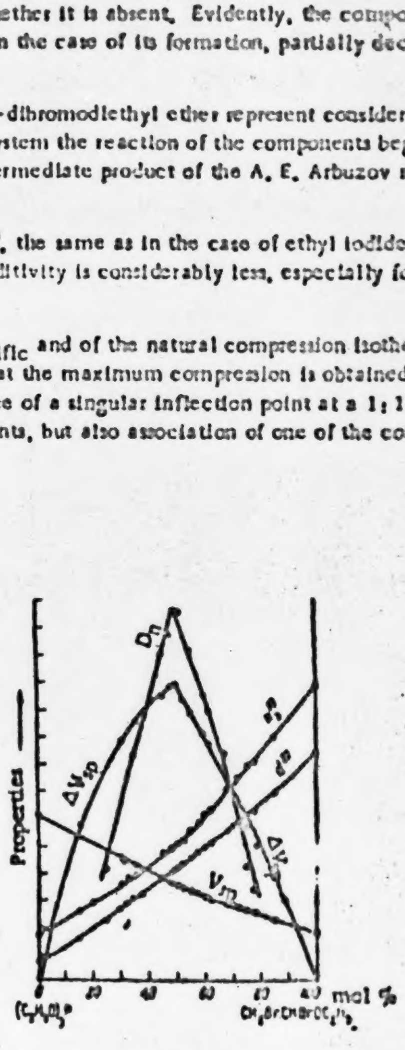

Fig. 4.

As a result, the data shown on the composition-property diagram for the system triethyl phosphite-α,β-dibromodiethyl ether support the presence of chemical reaction in the system, and in conjunction with the data obtained by V. S. Abramov [5], serve as proof that an intermediate addition product is formed in the process of rearranging triethyl phosphite to the ester of ethoxybromophosphinic acid.

That the obtained composition-property diagrams reflect in the given case the formation of an intermediate product, and not of the final rearrangement product, is indicated by the viscosity deviation of the system from additivity, which for the equimolar mixture is twice the deviation for the 1 : 1 triethyl phosphite-ethyl iodide mixture after heating at 50°.

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STABILITY OF CALCIUM HYDROSULFOALUMINATE IN PORTLAND CEMENT ROCK

Corresponding Member Acad. Sci. USSR P. P. Budnikov and V. S. Gorshkov

A substantial amount of calcium hydrosulfoaluminate—$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$—is formed in the hardening of Portland cement, in view of which the question as to the stability of this compound in the hardened Portland cement rock assumes great importance. For the most part the existing studies [1-3] discuss the question of the stability of the calcium hydrosulfoaluminate monocrystals obtained in the reaction of water solutions of calcium aluminates and gypsum.

In studying the crystals of calcium hydrosulfoaluminate under the microscope, O. M. Astreeva and L. Ya. Lopatnikova [1] [illegible] with time they decomposed under ordinary conditions into gypsum, aluminum hydroxide and calcium [illegible] stability of calcium hydrosulfoaluminate monocrystals, obtained by the same method, as a [illegible] change in the temperature and moisture content of the atmosphere, T. Yu. Lyubimova [2] came to the conclusion that this compound is stable only in an atmosphere saturated with water vapor at 18°.

Making a microscopic study of the calcium hydrosulfoaluminate preparations obtained by dissolving Portland cement in water and subsequently precipitating the calcium aluminates with $CaSO_4$ solution, Koyonagi [3] states that fine crystals are formed in the course of 2-3 months. Here supplementary chemical analysis methods revealed that the calcium hydrosulfoaluminate, formed in the cement rock, migrates with time into $4CaO\cdot Al_2O_3\cdot nH_2O$ and gypsum.

In studying the hydration products of Portland cement, containing from 2.75 to 16.5% SO_3, in the temperature interval from 25 to 100°, Kalousek and Adams, by the method of differential thermal analysis, revealed the formation of $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, and supposedly of the analogous calcium sulfoferrite, which then migrate into the corresponding solid solutions of these products, subsequently being transformed into phase X. In their opinion, phase X constitutes a gelatinous mass, containing all of the oxide components of the cement. From the presented survey it is obvious that the data on the question of the stability of calcium hydrosulfoaluminate, both that synthesized from solutions and that formed directly in hydrated cement, are contradictory and extremely limited.

In our study we used the chemical and x-ray methods to determine the stability of calcium hydrosulfoaluminate. Various methods were used to prepare the calcium hydrosulfoaluminate: 1) the use of water to mix the Portland cement, containing a large amount of gypsum; 2) the use of water to mix a mixture of finely dispersed $3CaO\cdot Al_2O_3$ and $CaSO_4\cdot 0.5H_2O$, taken in stoichiometric amounts to yield a calcium hydrosulfoaluminate with a high sulfate content; and 3) by the method of reacting water solutions of $3CaO\cdot Al_2O_3$ and $CaSO_4\cdot 0.5H_2O$.

By the first method, to obtain calcium hydrosulfoaluminate in a hardened cement mass, we took two Portland clinker cements of different mineralogical composition; clinkers from the "Giant" plant, containing 38% C_3S, 30% C_2S, 12% C_3A, 13% C_4AF, and clinkers from the "October" plant, containing 45% C_3S, 27% C_2S, 6% C_3A, 17% C_4AF. The cements were prepared by grinding the clinkers to a specific surface of 5100 sq.cm./g, and then adding finely pulverized gypsum half-hydrate in an amount equal to 6.35% SO_3. From the obtained cements we prepared specimens of a plastic consistency and composition 1 : 0 with a water-cement ratio equal to 0.52.

By the second method the tricalcium aluminate and gypsum half-hydrate, ground to a specific surface of about 7000 sq. cm./g, were mixed in stoichiometric proportions, mixed with 70% water, and from the obtained mixtures specimens were prepared, which after a day were shaped and placed in a medium saturated with water vapor at 20-22°, where they were kept for 18 months. The amount of unreacted gypsum in the cement rock and in the artificially prepared calcium hydrosulfoaluminate was periodically determined by the method of dissolving it in a saturated lime-water solution. The results of the determinations are given in Table 1.

TABLE 1

Kinetics for the Reaction of Gypsum With "Giant" and "October" Cements and Tricalcium Aluminate

Name of binder	Starting amount free SO_3, in %	Amount of unbound (free) gypsum, in % SO_3							
		1 day	3 days	7 days	14 days	28 days	3 months	12 months	18 months
"Giant" cement + + $CaSO_4 \cdot 0.5H_2O$	6.32	1.74	1.08	0.68	0.33	0	0	0	0
"Oct[illegible] + Ca[illegible]	[illegible]	[illegible]	1.77	1.23	0.90	0.03	0.21	0	0
$3CaO \cdot Al_2O_3$ + + $CaSO_4 \cdot 0.5H_2O$	[illegible]	[illegible]	6.10	4.32	2.81	2.03	0.07	0.02	0.18

From the data in Table 1 it can be seen that free gypsum is absent in the "Giant" cement after a 28-day hydration period, while the "October" cement completely assimilates the gypsum only after 3 months, the formation of calcium hydrosulfoaluminate from tricalcium aluminate and gypsum half-hydrate is also practically ended only after 3 months.

To determine the stability of calcium hydrosulfoaluminate at elevated temperatures the specimens from "Giant" cement, and also from tricalcium aluminate and gypsum half-hydrate, after 18 month hardening under moist conditions, were subjected to heat treatment in a medium saturated with water vapor at 30, 40, 60, 80 and 100° for 8 hours, and also to an autoclave treatment with the following regime: 2 hours to raise the pressure to 8 atm., holding at 8 atm. for 4 hours, and 2 hours to drop the pressure.

After the water-heat treatment the specimens were analyzed for the amount of free gypsum by the method of dissolving the gypsum in a saturated lime-water solution. The results of the determinations are given in Table 2.

TABLE 2

Amount of Free Gypsum in "Giant" Cement and in Synthetic Calcium Hydrosulfoaluminate

Name of binder	Starting amount of SO_3, in %		Amount of free SO_3 after treatment, in %					
	bound	free	at 30°	at 40°	at 60°	at 80°	at 100°	at 8 atm.
"Giant" cement	6.320	0	0	1.089	1.194	1.345	1.644	1.697
$3CaO \cdot Al_2O_3$ + gypsum	18.950	0.180	0.180	1.475	1.609	2.183	2.601	2.978

The data in Table 2 show that calcium hydrosulfoaluminate, stable at 20-22°, as the result of water-heat treatment begins to decompose with the liberation of free gypsum at a temperature of about 40°. Elevation of the temperature results in an increase in the amount of liberated gypsum. Portland cement rock and the calcium hydrosulfoaluminate, synthesized in the solid phase, after 18-month hydration under moist conditions, were subjected to x-ray phase analysis by the powder method. For this the powders, dehydrated with ethyl alcohol, were placed in a capillary with an internal diameter of 0.5 mm, and, using copper filtered radiation in a RDK chamber with a diameter of 57.3 mm, the pattern was taken with an exposure time of 12 hours. Here the voltage on the tube was 30 kv., and the anode current was 20 ma.

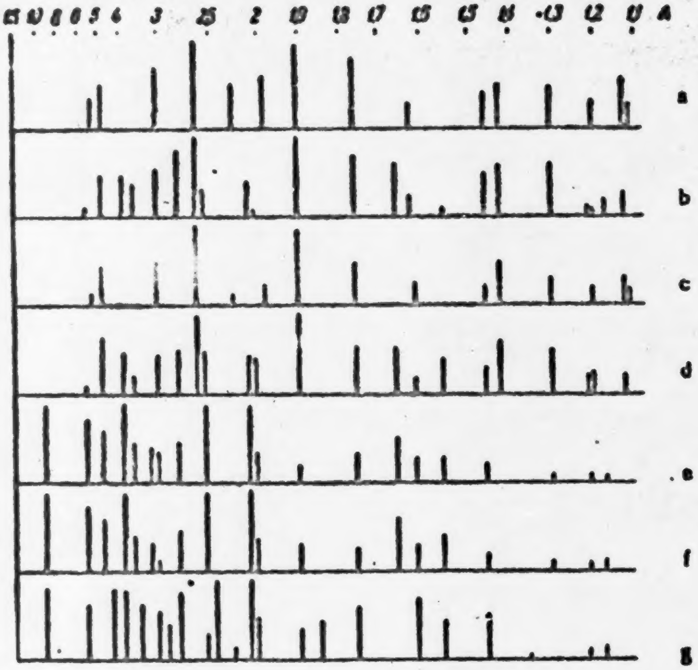

Fig. 1. Powder x-ray patterns of the hydrated cements and calcium hydrosulfoaluminate: a) "Giant" plant cement without gypsum b) the same cement with gypsum, c) "October" plant cement without gypsum, d) the same cement with gypsum, e) $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$, synthesized from solutions of $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot CaSO_4 \cdot 0.5H_2O$, f) calcium hydrosulfoaluminate, synthesized in the solid phase from $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$ prior to water heat treatment, g) the same compound after treatment at 40°.

The intensity of the diffraction lines and the values of the interplanar distances for the hydrated "October" and "Giant" cements are shown in Fig. 1.

In comparing the intensity of the diffraction lines and the values of the interplanar distances for the 18-month hydrated "Giant" and "October" cements, not containing gypsum in their composition, with the indices for the same cements, but containing gypsum (introduced in the mixing) it should be mentioned that in the latter, lines are present that characterize the high-sulfate form of calcium hydrosulfoaluminate. The "Giant" cement, containing 6.32% SO_3, in addition to the principal lines corresponding to the hydrated-mineral clinkers, shows additional lines at 3.87, 3.46, 2.53 and 2.11 A. For the "October" cement, containing 6.34% SO_3, the lines corresponding to $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ are at 3.85, 3.43, 2.74, 2.53, 2.14 and 1.56 A. Here for both the "Giant" and "October" cements a portion of the less intense lines, corresponding to calcium hydrosulfoaluminate, are superimposed on the lines of the other hydration products of the cement, in this way (enhancing) the intensity of the latter. Lines, characterizing the presence of free gypsum in any of its modifications, were not found on the x-ray patterns.

From this it follows that the phase analysis of two Portland cements of different mineralogical composition, after their joint hydration with gypsum for 18 months at 20-22°, does not show decomposition of the formed calcium hydrosulfoaluminate, which in turn is supported by the chemical analysis results (after 18 months of hydration both of the cements do not contain free gypsum).

Phase analysis of the calcium hydrosulfoaluminate, obtained in the solid phase from $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$, reveals that after keeping the specimens under moist conditions at 20-22° for 18 months the values of the interplanar distances (taking into account the error incurred in measuring the lines) are equal to the corresponding lines for the calcium hydrosulfoaluminate obtained by the method of reacting water solutions of $3CaO \cdot Al_2O_3$ and $CaSO_4 \cdot 0.5H_2O$ with subsequent removal after 7 days of the formed $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ crystals from the mother liquor, which can be seen in Fig. 1.

The "Giant" cement and the calcium hydrosulfoaluminate that had been synthesized in the solid phase, hydrated jointly with gypsum for 18 months, after 8-hour treatment at 30, 40, 60, 80 and 100° in a water vapor-saturated medium, and also after autoclaving, were subjected to x-ray analysis in order to establish the stability of calcium hy[illegible] at elevated temperatures. The phase analysis results agree with the data obtained by the chemical me[illegible] [illegible]ition point of calcium hydrosulfoaluminate — after water-heat treatment at 40° lines are [illegible], 3.06, 2.43, 2.35 and 1.97 A, characterizing the presence of $CaSO_4 \cdot 2H_2O$, for which the values of the interplanar distances correspond to those given in the table [5]. The decomposition character of the calcium hydrosulfoaluminate crystals is shown in Fig. 2 (see attachment to p. 1232).

The intensity of the lines, corresponding to gypsum, increases in measure with increase in the temperature of treatment, which is evidence that a large amount of gypsum is liberated in the decomposition of calcium hydrosulfoaluminate.

The following conclusions can be made on the basis of the performed study: 1) in a moist atmosphere at 20-22° the calcium hydrosulfoaluminate formed in cement rock is a stable compound; 2) calcium hydrosulfoaluminate begins to decompose when subjected to a water-heat treatment at 40°; 3) the decomposition of calcium hydrosulfoaluminate during water-heat treatment is accompanied by the liberation of free gypsum, the amount of which increases in measure with increase in the temperature.

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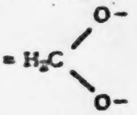
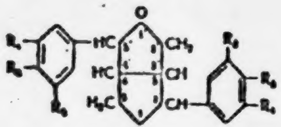
SYNTHESIS OF THE HEXAHYDRO-(3,4:3',4')-FUROFURAN SYSTEM – THE PRINCIPAL NUCLEUS OF NATURAL RESINOLS

N. B. Galstukhova

(Presented by Academician I. L. Knunyants, October 12, 1956)

The condensed heterocyclic hexahydro-(3,4:3',4')-furofuran system lies at the base of a definite group of natural substances, the so-called phenolic resinols or lignans.

Included among such compounds are: pinoresinol [(I), $R_1 = CH_3O$; $R_2 = OH$; $R_3 = H$], eudesmin [(I), $R_1 = R_2 = CH_3O$; $R_3 = H$], sesamin [(I), $R_1R_2 =$  $H_2C\begin{matrix}\diagup O-\\ \diagdown O-\end{matrix}$; $R_3 = H$] and syringaresinol [(I), $R_1 = R_3 = CH_3O$; $R_2 = OH$].

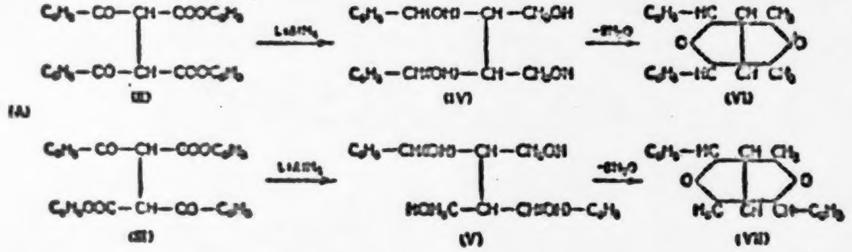


(I)

This series of substances represents definite interest from the viewpoint of biological activity; in particular, one of the members of this group of compounds, sesamin, shows bacteriostatic activity against pathogenic bacteria, especially against Mycobacterium tuberculosis, the growth of which is inhibited by sesamin at a dilution of $1:10^{-7}$ [1,2]. The insecticidal action of pyrethrin is also substantially enhanced by sesamin [3,4].

It seemed of interest to determine the possibility of synthesizing the principal nucleus of resinols, namely (I) – 2,5'-diphenylhexahydro (3,4:3',4') furofuran ($R_1 = R_2 = R_3 = H$), since only the aromatic derivatives of the hexahydrofurofurans are found in nature, having substituents in the benzene ring, the transition from which to compounds with other substituents is difficult.

To synthesize 2,5'-diphenylhexahydro (3,4:3',4') furofuran we selected scheme (A), which is also applicable to the synthesis of compounds with substituted benzene rings, and accomplished by this scheme the synthesis of both 2,5'-diphenylhexahydro (3,4:3',4') furofuran and its structural isomer, the 2,5-diphenyl derivative.



The starting substance in the synthesis of the 2,5'- and 2,5-diphenylhexahydro (3,4:3'4') furofurans was the dibenzoylsuccinic ester, obtained by the Knorr method [5] as two isomers: the β-ester (m.p. 123-130°) and the γ-ester (m.p. 74-75°).

After the reduction of these compounds to the corresponding tetrahydric alcohols it could be expected that the isomeric tetraols would be formed. The cleavage of water from the latter leads to 2,5'-diphenylhexahydro (3,4:3',4') furofuran and 2,5-diphenylhexahydro (3,4:3',4') furofuran, respectively.

The reduction of the β-isomer of the dibenzoylsuccinic ester with lithium aluminum hydride in ether at 0° led to obtaining β-2,3-di (α-hydroxybenzyl)-1,4-butanediol, called the β-tetraol (IV), in 50% yield on the β-dibenzoylsuccinic ester. Prisms from dichloroethane, m.p. 137-138.5°.

Found %: C 71.82; H 7.58; OH 22.25. $C_{18}H_{22}O_4$. Calculated %: C 71.52; H 7.28; OH 22.50.

Tetraacetate, m.p. 112-113°.

Found %: C 65.98; H 6.47; $COCH_3$ 31.8. $C_{26}H_{30}O_8$. Calculated %: C 66.38; H 6.38; $COCH_3$ 36.6.

Tetrabenzoate, m.p. 258-259°.

Found %: C 76.44; [illegible] Calculated %: C 76.88; H 5.20.

The γ-dibenzoylsuccinic ester was reduced with lithium aluminum hydride under the same conditions as the β-isomer. We obtained γ-2,3-di (α-hydroxybenzyl)-1,4-butanediol (V), called the γ-tetraol, in 31% yield on the γ-dibenzoylsuccinic ester. Colorless prisms from dichloroethane with m.p. 147.5-148°.

Found %: C 71.56; H 7.26; OH 23.38. $C_{18}H_{22}O_4$. Calculated %: C 71.52; H 7.28; OH 22.50.

In the reduction of the racemic dibenzoylsuccinic ester it was possible to obtain three racemates of 2,3-di (α-hydroxybenzyl)-1,4-butanediol, while from the meso dibenzoylsuccinic ester it was possible to obtain two meso forms and one racemate.

We were able to isolated from the reduction products both the β- and γ-tetraol forms as a single crystalline tetrahydric alcohol. The oily substances remaining after their separation also contained hydroxyl groups; it is possible that the other isomers were found in them.

We subjected the obtained β- and γ-tetraol isomers to dehydration. Dehydration of the tetraol, obtained by the reduction of the meso dibenzoylsuccinic ester, should yield 2,5-diphenylhexahydro (3,4:3',4') furofuran, since only in this case does closure of one of the tetrahydrofuran rings leave the remaining primary alcohol groups in the cis-position to each other. In like manner the tetraol, obtained by the reduction of the racemic dibenzoylsuccinic ester, should give 2,5'-diphenylhexahydro (3,4:3',4') furofuran. We ran the cleavage of water from the β-tetraol in vacuo at a residual pressure of 9 mm and a bath temperature of 110-170° in the presence of potassium bisulfate. After the separation of water had ceased the main portion of the substance distilled as a yellow sirup with b.p. 220-230° at 9 mm. Rubbing with dry ether caused the substance to crystallize. The isolated substance, recrystallized from alcohol, had m.p. 88.5-90°, and from the elementary analysis corresponded to the composition of diphenylhexahydro (3,4:3',4') furofuran, called the β-bicycle; the substance did not contain any hydroxyl groups, as shown by the analytical determinations and by a study of the infrared spectrum. The yield was 54%.

Found %: C 81.09; H 6.69. $C_{18}H_{18}O_2$. Calculated %: C 81.21; H 6.77.

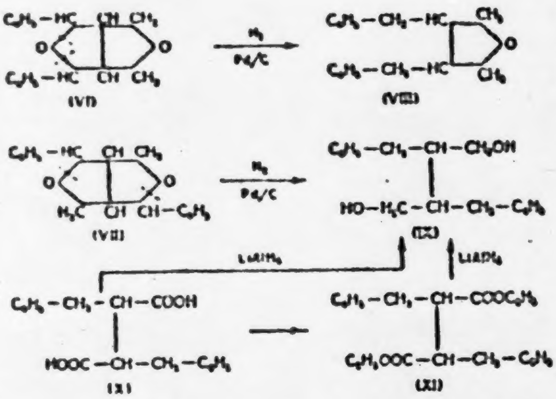
The γ-tetraol was also dehydrated by the method of slow heating in the presence of potassium bisulfate at a bath temperature of 150-200° and a vacuum of 13 mm. The diphenylhexahydro (3,4:3',4') furofuran, called the γ-bicycle, distilled at 13 mm and 220-230° as a viscous reddish-orange oil, which when cooled and treated with dry ether crystallized as thin needles; from alcohol, m.p. 72.5-74.5°, yield 25.6%.

Found %: C 81.29; H 7.04. $C_{18}H_{18}O_2$. Calculated %: C 81.21; H 6.77.

The Tserevitinov determination and the infrared spectrum of the compound revealed the absence of hydroxyl groups.

To identify the 2,5- and 2,5'-diphenylhexahydro (3,4:3',4') furofurans synthesized by us and to determine the position of substituents in them we undertook the catalytic hydrogenation of these compounds in glacial acetic acid in the presence of palladium-on-carbon at atmospheric pressure and room temperature. Here, due to the influence of phenyl groups, rupture of the ether linkage occurs between the oxygen and the secondary carbon atoms [scheme (B)], as was shown experimentally, for example, in the case of the reductive cleavage of 2-phenyldioxane and 2,3-diphenyldioxane [6].

(B)



Hydrogenation of the β-bicycle under the conditions indicated above gave a substance with m.p. 65.5-67°, yield 79%. From the analysis data and the absence of hydroxyl groups (Tserevitinov determination) this compound was 2,3-dibenzyltetrahydrofuran (VIII).

Found %: C 85.64; H 7.92. $C_{18}H_{20}O$. Calculated %: C 85.71; H 7.94.

Consequently, the β-bicycle is 2,5-diphenylhexahydro (3,4:3',4')-furofuran (VI).

The γ-bicycle was hydrogenated under the same conditions; here we obtained a viscous oily substance, which crystallized after drying *in vacuo* and rubbing with dry ether. The dl-2,3-dibenzyl-1,4-butanediol (IX), isolated in 49% yield, had m.p. 87-88° (from ligroin); its mixed melting point with the dl-2,3-dibenzyl-1,4-butanediol, obtained by the reduction of dl-2,3'-dibenzylsuccinic acid with lithium aluminum hydride, was not depressed.

Found %: C 80.19; H 7.92; OH 13.07. $C_{18}H_{22}O_2$. Calculated %: C 79.90; H 8.20; OH 12.60.

Diacetate, m.p. 73.5-74.5° (from alcohol).

Found %: C 74.92; H 7.53. $C_{22}H_{26}O_4$. Calculated %: C 74.53; H 7.40.

The structure of the dl-2,3-dibenzyl-1,4-butanediol was shown by the counter synthesis, proceeding from either dl-2,3-dibenzylsuccinic acid (X) [7] or its diethyl ester (m.p. 80-81.5°) (XI), which were reduced with lithium aluminum hydride in ether. After the usual treatment we obtained an oily substance that crystallized with difficulty. Vacuum-distillation at 195-210° and 1.6 mm gave a crystalline compound, m.p. 87-88°.

Found %: C 79.82; H 8.17. $C_{18}H_{22}O_2$. Calculated %: C 79.90; H 8.20.

As a result, we confirmed the structure of the racemic 2,3-dibenzyl-1,4-butanediol (IX), and consequently showed the structure of the γ-bicycle synthesized by us as being 2,5'-diphenylhexahydro (3,4:3',4')furofuran (VII).

I wish to express my deep gratitude to my research director, Prof. M. N. Shchukina, for his valuable counsel and untiring attention in the execution of the present study.

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THE CLAISEN REARRANGEMENT IN THE ALLYL ARYL SULFIDE SERIES

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(Presented by Academician A. V. Topchiev, December 24, 1956)

The Claisen rearrangement, an isomerization that is characteristic for allyl aryl ethers, in the opinion of some investigators [1], is also inherent to their sulfur analogs. This conclusion is based on the study of Hurd and Greengard [2], where the authors, in studying the pyrolysis of allyl phenyl sulfide and allyl p-tolyl sulfide, found that here the corresponding o-allylthiophenol and 2-allyl-4-methylthiophenol are formed in about 25% yield.

In contrast to [2], we established that practically no allylthiophenol is formed when allyl phenyl sulfide is boiled without solvent, but instead the allyl phenyl sulfide is isomerized to propenyl phenyl sulfide, identical with the product isolated by Tarbell and McCall [3] when they treated allyl phenyl sulfide with an alcoholic solution of a sodium alcoholate. On standing or when heated, propenyl phenyl sulfide forms condensation products; the compound, assumed [2] to be o-allylthiophenol, apparently represented condensation products of the propenyl phenyl sulfide, containing a certain amount of monomer and only traces of the allylthiophenol, which up to now has remained unknown. The thermal isomerization of allyl o-tolyl and allyl p-tolyl sulfides proceeds in the same manner as for allyl phenyl sulfide, and here the propenyl o-tolyl and propenyl p-tolyl sulfides are respectively obtained; in this connection neither allyl-p-thiocresol (in contradiction to [2]) nor allyl-o-thiocresol is formed. The propenyl tolyl sulfides were also obtained by us as the result of heating the corresponding allyl tolyl sulfides with an alcoholic solution of a sodium alcoholate by the Tarbell-McCall method [3]. The thermal isomerization of allyl aryl sulfides proceeds by the scheme

$$\mathrm{ArS-CH_2CH=CH_2 \xrightarrow{} ArSCH=CHCH_3;\quad (Ar=C_6H_5,\quad o\text{-}C_6H_4CH_3\ и\ n\text{-}C_6H_4CH_3).}$$

The structure of the thermal isomerization products of allyl aryl sulfides was established by the method of their reductive desulfurization over Raney Ni; here the propenyl phenyl sulfide suffers cleavage to yield propane and benzene, while the propenyl tolyl sulfides suffer cleavage to yield propane and toluene.

In a typical experiment 150 g of allyl phenyl sulfide was boiled under reflux in a nitrogen stream for 9 hours. The mixture was repeatedly treated with 20% NaOH solution; the alkaline water layer contained only traces of mercaptans—after suitable treatment we obtained 0.19 g of lead mercaptide. After separating from the alkaline water layer the organic layer was diluted with petroleum ether, dried, and distilled through a column with an efficiency of 25 theoretical plates. Here we isolated 39.7 g of propenyl phenyl sulfide, or a yield of 36% based on reacted allyl phenyl sulfide, b.p. 79-80°/3 mm, 225-226°/740 mm, n_D^{20} 1.5850; d_4^{20} 1.0323.

Found %: C 72.04; H 6.68; S 21.32. $C_9H_{10}S$. Calculated %: C 72.00; H 6.67; S 21.34.

We recovered 40 g of allyl phenyl sulfide.

A solution of 5 g of propenyl phenyl sulfide in 75 ml of glacial acetic acid was oxidized with a 200% H_2O_2 for 1 hour at 100°. The mixture was diluted with water and evaporated to ~ 50 ml, which operation was repeated five times, after which, cooling in an ice-salt mixture gave a precipitate of propenyl phenyl sulfone (probably the trans-isomer), yield 34.1%, m.p. 68.5-69° (from alcohol + water in a 4:1 ratio).

Found %: C 59.36; H 5.46; S 17.70. $C_9H_{10}SO_2$. Calculated %: C 59.34; H 5.49; S 17.58.

The mother liquors from the trans-propenyl phenyl sulfone were extracted with benzene, and the extracts were vacuum-distilled to give propenyl phenyl sulfone (probably the cis-isomer), yield 17.0%, b.p. 176-180°/3.5 mm (bath temperature), $n_D^{21.8}$ 1.5536.

Found %: C 59.31; H 5.55; S 17.54. $C_9H_{10}SO_2$. Calculated %: C 59.34; H 5.49; S 17.58.

Starting from o-thiocresol, allyl o-tolyl sulfide was obtained in 90% yield by the method recommended in [2] for the preparation of allyl phenyl sulfide, b.p. 96-97°/5 mm, n_D^{20} 1.5707; d_4^{20} 1.0125.

Found %: C 73.17; H 7.42; S 19.04. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51.

Six grams of allyl o-tolyl sulfide was oxidized with H_2O_2 in the same manner as before; after benzene extraction and vacuum-distillation the allyl o-tolyl sulfone was isolated, yield 61%, b.p. 168-170°/3 mm, n_D^{20} 1,5492; d_4^{20} 1.1673.

Found %: C 61.42; H 6.17; S 16.17. $C_{10}H_{12}SO_2$. Calculated %: C 61.22; H 6.12; S 16.32.

Twelve grams of [illegible] boiled under reflux in a nitrogen stream for 3 hours. The reaction mixture was worked up in the same manner as in the case of allyl phenyl sulfide. After two distillations from a Claisen flask we obtained 6.15 g (51.2% of theory) of propenyl o-tolyl sulfide, b.p. 129-133°/25 mm, n_D^{20} 1,5762; d_4^{20} 1.0175.

Found %: C 73.32; H 7.29; S 19.91. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51.

Three grams of propenyl o-tolyl sulfide was oxidized with H_2O_2 in CH_3COOH in the same manner as before. Here we obtained 2,5 g of propenyl o-tolyl sulfone, b.p. 173-175°/7 mm, n_D^{23} 1,5551; d_4^{23} 1.1741.

Found %: C 61.24; H 6.15; S 16.43. $C_{10}H_{12}SO_2$. Calculated %: C 61.22; H 6.12; S 16.32.

Allyl p-tolyl sulfide (7.2 g) was boiled under reflux in a nitrogen stream for 3 hours. Here partial decomposition was observed and ~ 0.33 g of propylene was evolved. The reaction mixture was worked up in the same manner as for the o-isomer, and the propenyl p-tolyl sulfide was isolated in 36.6% of the theoretical yield, b.p. 131-136°/25 mm, n_D^{20} 1.5746; d_4^{20} 1.0119.

Found %: C 73.24; H 7.32; S 19.43. $C_{10}H_{12}S$. Calculated %: C 73.17; H 7.32; S 19.51.

The product does not give a precipitate with a solution of $Pb(CH_3COO)_2$ in alcohol, while the higher boiling fractions and the residue from the distillation contain only traces of compounds with SH-group.

Two grams of propenyl phenyl sulfide in 112 ml of alcohol was boiled with stirring for 8 hours with the Raney Ni obtained by the method of [4] from 70 g of Raney alloy. The evolved gases were collected in a Mariotte flask and analyzed to give 278 ml of propane, or 96% of the theoretical yield. The reaction mixture was diluted with 50 ml of water and distilled from Ni and NiS. The distillate was distilled through a column 38 cm high with a fine Levina metal packing. The fractions with b.p. 64,5-77° (containing an azeotropic mixture), after dilution with water, gave 0,5 ml of benzene (42% of theory), identified by its absorption spectrum in the ultraviolet region.

The reduction of 5 g of propenyl o-tolyl sulfide with Raney Ni (from 140 g of Raney alloy) in 280 ml of alcohol (boiling for 12 hours), the same as before, gave 1.9 g (78% of theory) of toluene, b.p. 107-109°, n_D^{21} 1,4910.

Six grams of propenyl p-tolyl sulfide was reduced with Raney Ni (from 160 g of the alloy) in 300 ml of alcohol, the same as described above. We isolated 654 ml of propane (81% of theory) and 1,4 g of toluene (4 of theory), b.p. 105-109°, $n_D^{22.5}$ 1,4779.

The color reaction with sulfuric acid is characteristic for propenyl aryl sulfides studied by us: two drops of concentrated H_2SO_4 are added to a drop of the propenyl aryl sulfide to give a red coloration, which rapidly turns to a brown. The allyl aryl sulfides give only a light-yellow color when treated with concentrated H_2SO_4.

The data obtained by us permit the conclusion that for the allyl aryl thioethers, in contrast to the corresponding oxygen compounds, the Claisen rearrangement is practically nonexistent. When heated, the allyl aryl thioethers isomerize to the corresponding propenyl aryl sulfides.

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STUDY OF THE MECHANISM OF THE ALKYLATION OF AMINES WITH N-TRIMETHYL-α-PHENETHYLAMMONIUM IODIDE

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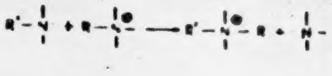
It is known that ammonium salts of type $Ar-CH_2-\overset{\oplus}{N}\equiv$ are capable of alkylating primary and secondary amines through the transfer of the $ArCH_2$ radical from one nitrogen atom to another [1-3,5].

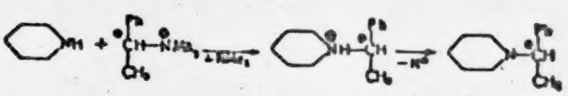
The alkylation of amines with ammonium compounds is of interest in view of the fact that the final and starting substances in this reaction belong to the same class of compounds:



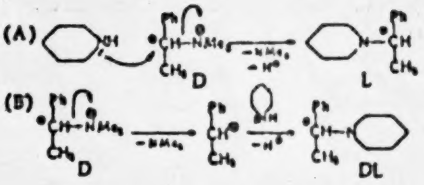
$$R'-\overset{|}{\underset{|}{N}} + R-\overset{|}{\underset{|}{N}}{}^{\oplus}- \longrightarrow R'-\overset{|}{\underset{|}{N}}{}^{\oplus}-R + \overset{|}{\underset{|}{N}}-$$

The mechanism of this reaction has not been studied up to now.

We studied the alkylation of piperidine and morpholine with optically active N-trimethyl-α-phenethylammonium iodide:



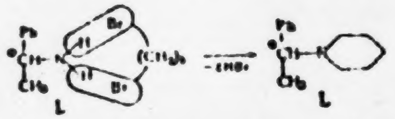
This reaction can proceed [4] either by the synchronous mechanism [scheme (A)], or by the asynchronous mechanism with the intermediate formation of the free carbonium ion [scheme (B)]:



If the reaction proceeds by the synchronous mechanism [scheme (A)] the obtained N-α-phenethylpiperidine should possess optical activity. If the reaction proceeds through the intermediate formation of the free carbonium ion [scheme (B)] the obtained product should not possess optical activity.

It was found that the optical activity of the phenethyl radical is retained in the substitution process: the N-α-phenethylpiperidine obtained from the D-salt was levorotatory, while the N-α-phenethylmorpholine obtained from the L-salt was dextrorotatory. From this it follows that the reaction proceeds by the synchronous mechanism.

Since the configuration of the optically active N-α-phenethylpiperidines had not been established up to now, the need arose to determine the configuration of the levorotatory N-α-phenethylpiperidine obtained by us. For this we synthesized l-N-α-phenethylpiperidine by a method where the configuration at the carbon atom did not change during the reaction process. We proceeded from l-α-phenethylamine, which was reacted with 1,5-dibromopentane to yield N-α-phenethylpiperidine, also possessing levo rotation:

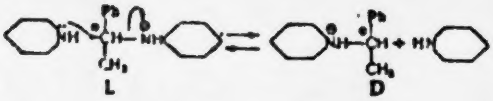


Since the asymmetric center is not touched in the utilized reaction, it can be stated that levorotatory N-α-phenethylpiperidine belongs to the L-series.

From this it follows that the configuration of the α-phenethyl radical shows inversion in the reaction of d-N-trimethyl-α-phenethylammonium iodide with piperidine (and apparently, also with morpholine).

It was also found that the optical purity of the N-α-phenethylpiperidine, obtained in the alkylation of piperidine with d-N-trimethyl-α-phenethylammonium iodide, depends on the reaction time. When the heating was for 12 hours at 125° the obtained N-α-phenethylpiperidine showed a specific rotation of $\alpha_D^{19} = -7.5°$, while when the heating was for 3 hours at the same temperature the obtained substance had a specific rotation of $\alpha_D^{20} = 15.6°$.

Apparently, a reduction in the optical purity during heating was due to the secondary reaction of symmetrical substitution:



It is evident that constant repetition of this process should eventually lead to racemization.

EXPERIMENTAL

1. Reaction of d-N-trimethyl-α-phenethylammonium iodide with piperidine. A mixture of 0.1 mole of d-N-trimethyl-α-ammonium iodide [4] and 0.3 mole of piperidine was heated in a nitrogen atmosphere for 12 hours at 125°. The reaction products were dissolved in 100 ml of water, and the resulting solution was made alkaline and extracted with benzene. The benzene extract was dried over powdered potassium hydroxide.

Distillation of the material through a column gave: 6.47 g of d-N-dimethyl-α-phenethylamine with b.p. 66-70° (8 mm), n_D^{19} 1.5032; d_4^{18} 0.9054, $[\alpha]_D^{19} = 69.0°$ (corresponds to an optical purity of 95%) and 5.47 g of N-α-phenethylpiperidine with b.p. 118-119° (9 mm), n_D^{19} 1.5292; d_4^{19} 0.9622, $[\alpha]_D^{19} = -7.5°$ (in methanol, c = 8.1).

In a similar reaction, where the reaction time was 3 hours, we obtained 3.00 g of N-α-phenethylpiperidine. B.p. 118-119° (9 mm), n_D^{19} 1.5279; d_4^{20} 0.9604, $[\alpha]_D^{19} = -15.6°$ (in methanol, c = 9.1).

2. Preparation of l-N-α-phenethylpiperidine. A mixture of 0.1 mole of l-α-phenethylamine* (in three volumes of ether) and 0.042 mole of 1,5-dibromopentane [6] was placed in a flask, which was connected to a Vigreaux column fitted with a total reflux head. The ether was slowly distilled off by heating on the water bath. Reaction began after about half of the ether had been distilled off. The heating was terminated after 6 hours, and the flask contents were treated with 30 ml of 15% hydrochloric acid. The neutral substances were extracted with benzene. The aqueous solution was made alkaline with 8N NaOH, and the obtained free base was extracted with benzene.

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* Obtained by the literature method [7], $d_D^{20} = -39.8°$.

Distillation gave 6,93 g of l-α-phenethylamine with b.p. 68-69° (8 mm) and 7,43 g of l-N-α-phenethylpiperidine with b.p. 114-114,5° (7 mm). The latter substance had the following constants: d_4^{20} 0,9600; n_D^{20} 1,5268, $[\alpha]_D^{20}$ = − 33,0° (in methanol, c = 7,2). Picrate, m.p. 178-178,5°.

Found %: C 82,32; H 10,14. $C_{13}H_{19}N$. Calculated %: C 82,48; H 10,12.

3. Reaction of l-N-trimethyl-α-phenethylammonium iodide with morpholine. A mixture of 0,1 mole of l-N-trimethyl-α-phenethylammonium iodide* and 0,4 mole of morpholine was heated in a nitrogen atmosphere at 135° for 4,5 hours. The reaction mixture was dissolved in water and made alkaline with 8N NaOH. The separated oil was extracted with benzene. The benzene extract was dried over potassium hydroxide. The reaction products were distilled through a Vigreaux column 120 mm in length.

We obtained 6,9 g of N-dimethyl-α-phenethylamine with b.p. 68,5-69,5° (8 mm), n_D^{20} 1,5027; d_4^{20} 0,9032, $[\alpha]_D^{20}$ (in methanol) − 29.8° and 6,32 g of N-α-phenethylmorpholine, for which the following constants were found: b.p. 123-123,5° (8 mm), d_4^{20} 1,028, n_D^{20} 1,5278, $[\alpha]_D^{20}$ = + 16,2° (in 90% ethanol, c = 14,6).

Calculated on the basis of these data the specific rotation for pure N-α-phenethylmorpholine should be not less than +26,6°.

In a similar manner the reaction of dl-N-trimethyl-α-phenethylammonium iodide with morpholine gave dl-N-α-phenethylmorpholine. B.p. 128-9° (10 mm), d_4^{20} 1,018; n_D^{20} 1,5272, picrate, m.p. 194-194,5°.

Found %: C 75,25; H 8,96; N 7,55. $C_{12}H_{17}ON$. Calculated %: C 75,33; H 8,96; N 7,32.

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*Optical purity 61%.

2,4-DIMETHYL-1,3-PENTADIENE IN THE SYNTHESIS OF ALKANES WITH TWO TERTIARY CARBON ATOMS, SEPARATED BY A CH_2 GROUP (DITERT-ALKYLMETHANES)

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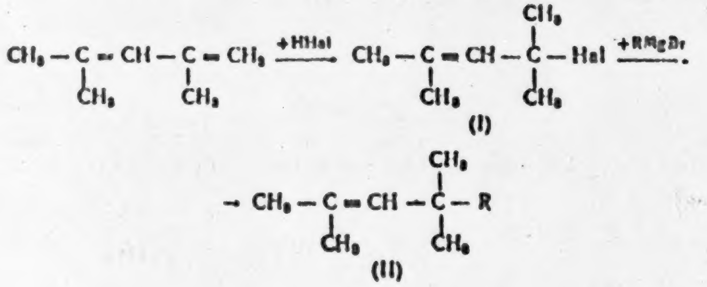
(Presented by Academician A. N. Nesmeyanov, December 21, 1956)

In previous communications [1,2] we described a method for the synthesis of ethylene hydrocarbons with a tertiary carbon atom, consisting in the reaction of alkylmagnesium bromides with tertiary bromides of the allyl type; the latter are easily obtained by the hydrobromination of branched diene hydrocarbons with a conjugated system of double bonds.

Thus, for example, the hydrobromide of 2,4-dimethyl-1,3-pentadiene (I; Hal = Br) served as the starting substance for the synthesis of 2,4,4-trimethyl-2-alkenes [1]: *



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{+HHal} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Hal \xrightarrow{+RMgBr}$$

(I)

$$\rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-R$$

(II)

In the present study, using the same 2,4-dimethyl-1,3-pentadiene as the starting material, we developed a new and convenient method for the synthesis of the difficultly accessible paraffin hydrocarbons with two tertiary carbon atoms, separated by a CH_2 group—the ditertalkylmethanes (only the first member of this series of hydrocarbons, 2,2,4,4-tetramethylpentane, is described in the literature [3]). The above indicated reaction was the first step of this synthesis, in which connection the replacement of the bromide by the hydrochloride of 2,4-dimethyl-1,3-pentadiene (I; Hal = Cl) made it possible to increase the yield of the 2,4,4-trimethyl-2-alkenes (II) from 30 to 45-50%, based on consumed chloride.

Alkenes (II) (R = CH_3, C_2H_5, C_3H_7, C_4H_9), already having one tertiary carbon atom, were then treated with hydrochloric acid to yield the saturated tertiary chlorides, the 2-chloro-2,4,4-trimethylalkanes (III; yield 90 %, which were then reacted with organomagnesium compounds in the presence of mercuric chloride (the catalyst in the Grignard-Wurtz reaction when RMgBr is reacted with tertiary chlorides [4,5]); the products of this last synthesis step were the alkanes with two tertiary carbon atoms, separated by a CH_2 group (IV; ditert-alkylmethanes):

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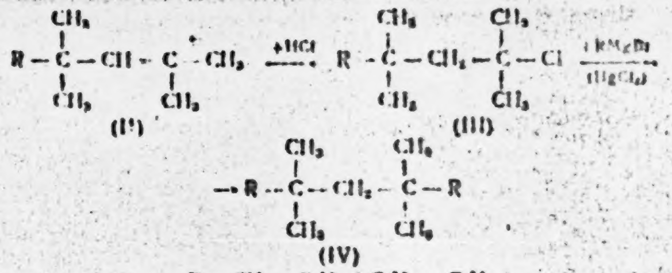
* The 3,5-dimethyl-5-ethyl-3-alkenes were obtained from 3,5-dimethyl-2,4-heptadiene in the same manner [2].



(II) (III) (IV)

$$R-C(CH_3)_2-CH=C(CH_3)-CH_3 \xrightarrow{+HCl} R-C(CH_3)_2-CH_2-C(CH_3)_2-Cl \xrightarrow[(MgClBr)]{+RMgBr} R-C(CH_3)_2-CH_2-C(CH_3)_2-R$$

$R = CH_3, C_2H_5, C_3H_7, C_4H_9$

In the reaction with organomagnesium compounds the saturated tertiary chloride (III) also cleaved hydrogen chloride, forming the starting alkenes (II) in 50-55% yield, which were used again for the synthesis of the alkanes (IV). Alkenes (II) and alkanes (IV) are easily separated by distillation. The yield of the alkanes was 15-25%, based on tertiary chloride taken for reaction, and 30-50%, based on consumed chloride.

EXPERIMENTAL

Hydrochlorination of 2,4-dimethyl-1,3-pentadiene. The unsaturated monohydrochloride of 2,4-dimethyl-1,3-pentadiene (I) was obtained by bubbling dry hydrogen chloride (to a weight increase of 37 g) into the diene hydrocarbon (93 g, 1 mole : b.p. 92-93°/745 mm; n_D^{22} 1.4445; d_4^{22} 0.7375; literature data [6]: b.p. 93-94°/755 mm, n_D^{20} 1.4448; d_4^{20} 0.7376), cooled in a mixture of ice and salt. During distillation and when stored, the hydrochloride, similar to the hydrobromide [1], cleaved hydrogen halide and to a substantial degree was converted to the starting diene and its dimer. For this reason we used the dried, but not distilled, hydrochloride, directly after its preparation, to obtain the alkenes (II).

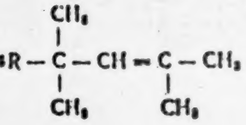
Synthesis of 2,4,4-trimethyl-2-alkenes (II). To an ether solution of the alkylmagnesium bromide (1.5 moles of alkyl bromide, 36 g of magnesium and 300 ml of absolute ether) was gradually added with ice-water cooling an ether solution of the monohydrochloride of 2,4-dimethyl-1,3-pentadiene (obtained from 1 mole of the diene).

After this reaction mixture was heated for 5 hours; dilute hydrochloric acid (2N) was used for the decomposition.

The yields of the alkenes, based on starting dimethylpentadiene, were 45-50%; their constants are given in Table 1.

TABLE 1

2,4,4-Trimethyl-2-alkenes



$$R-C(CH_3)_2-CH=C(CH_3)-CH_3$$

R	Name	B. p. °C/mm	n_D^{20}	d_4^{20}	Literature data [1]		
					B. p. °C/mm	n_D^{20}	d_4^{20}
CH_3	2,4,4-trimethyl-2-pentene	102—103/740	1.4131	0.7193	103—104/750	1.4130	0.7191
C_2H_5	2,4,4-trimethyl-2-hexene	130—131/752	1.4261	0.7433	129—130/755	1.4264	0.7437
C_3H_7	2,4,4-trimethyl-2-heptene	45—46/15	1.4310	0.7553	151—152/758	1.4307	0.7560
C_4H_9	2,4,4-trimethyl-2-octene	60—61/13	1.4360	0.7621	58.5—59/13	1.4356	0.7623

In all of the experiments the 2,4-dimethyl-1,3-pentadiene dimer with b.p. 90°/10 mm was isolated from the higher boiling fractions.

Hydrochlorination of 2,4,4-trimethyl-2-alkenes. The synthesized alkenes were saturated with hydrogen chloride with ice-salt cooling and then were shaken for 15-20 hours at room temperature with concentrated hydrochloric acid, saturated with hydrogen chloride under cooling. The obtained tertiary chlorides (III; 2-chloro-2,4,4-trimethylalkanes) were washed with water, dried over calcium chloride, and vacuum-distilled (yield 90%); their constants and the analysis data are given in Table 2.

TABLE 2

2-Chloro-2,4,4-trimethylalkanes

Name	B. p. °C/mm	n_D^{20}	d_4^{20}	MR_D		Found %			Calculated %		
				found	calc.	C	H	Cl	C	H	Cl
2-Chloro-2,4,4-trimethylpentane*	40—40.5/12	1.4302	0.8746	44.01	44.01	—	—	—	—	—	—
2-Chloro-2,4,4-trimethylhexane	55—56/10	1.4303	0.8768	48.79	48.63	66.60 66.53	11.84 11.97	21.75 21.63	66.46	11.77	21.79
2-Chloro-2,4,4-trimethylheptane	73—74/15	1.4448	0.8785	53.50	53.25	67.99 68.10	12.04 12.04	20.03 20.17	67.98	11.99	20.06
2-Chloro-2,4,4-trimethyloctane	90—90.5/12	1.4400	0.8065	57.74	57.86	69.46 69.43	12.17 12.08	18.53 18.43	69.26	12.15	18.59

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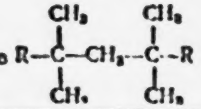
* Literature data for 2-chloro-2,4,4-trimethylpentane [3]: b.p. 53°/20 mm; n_D^{20} 1.431. The other chlorides are new.

TABLE 3

Alkanes of General Structure  (Ditert-alkylmethanes)

$$R-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-R$$

R	Name	F. p.	B. p. °C/mm	n_D^{20}	d_4^{20}	MR_D		Found %		Calculated %	
						found	calc.	C	H	C	H
CH_3	2,2,4,4-tetramethylpentane*	−66.2° (±2°)	120.7–121.3 (745)	1.4070	0.7198	43.75	43.76	—	—	—	—
C_2H_5	3,3,5,5-tetramethylheptane	Glass below −70°	61/8	1.4309	0.7660	52.76	53.00	84.66 84.65	15.34 15.34	84.82	15.18
C_3H_7	4,4,6,6-tetramethylnonane	Glass below −85°	84/9	1.4378	0.7813	62.05	62.33	84.84 84.87	15.14 14.98	84.70	15.30
C_4H_9	5,5,7,7-tetramethylundecane	Glass below −95°	106/7	1.4420	0.7934	71.30	71.47	84.79 84.70	15.23 15.27	84.80	15.20

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* Literature data for 2,2,4,4-tetramethylpentane [3] (obtained by the reaction of dimethylzinc with 2-chloro-2,4,4-trimethylpentane): f.p. −66.9; −67.1°; b.p. 122.3/ /760 mm; n_D^{20} 1.4069; d_4^{20} 0.7195. The other hydrocarbons are new.

Synthesis of ditert-alkylmethanes (IV) from tertiary chlorides (2-chloro-2,4,4-trimethylalkanes). To an ether solution of the organomagnesium compound (1.1 mole of alkyl bromide, 24.3 g of magnesium and 220 ml of absolute ether) was added 4 g of mercuric chloride, and after the latter had dissolved completely, the tertiary chloride (0.5 mole) was added very slowly (in 6 hours) with constant stirring and cooling of the reaction mixture to 13-15°. Then the stirring was continued for another 5 hours at room temperature and for 2 hours at 30-35°;

the reaction mixture was decomposed with dilute hydrochloric acid (2N). After distilling off the ether from the washed and dried ether extract the residue was boiled for 2 hours with sodium, distilled from the sodium, and then fractionally distilled through a column. Here the fractions removed were the starting 2,4,4-trimethyl-2-alkene (this fraction, the yield of which was 50-55% in all cases, was reused for the synthesis of the corresponding alkane) and a much higher boiling fraction of the alkane—the ditert-alkylmethane). The yields of the alkanes ranged from 15% (R = C_4H_9) to 25% (R = CH_3), based on tertiary chloride taken for reaction, or from 30 to 50%, based on consumed chloride; the constants and analysis data are presented in Table 3.

TABLE 4

Raman Spectra of Ditert-alkylmethanes

2,2,4,4-Tetramethylpentane	217 (0.5), 262 (1; b), 311–329 (1.5; b), 349 (0.3), 376 (1), 430 (0.5), 498 (0), 556 (3), 645 (1), 678 (1.5), 734 (18), 769 (0.5), 812 (0.5), 862 (1.5), 875 (4), 919 (5), 930 (3), 998 (0.3), 1022 (0.3), 1073 (0.5), 1107 (1), 1144 (2.5), 1173 (3.5), 1196 (2.5), 1242 (12), 1325 (0.5), 1333 (1), 1443 (10), 1465 (2.5).
3,3,5,5-Tetramethylheptane	257 (0), 329 (1), 387 (1), 406 (0), 445 (0), 474–490 (2; db), 544 (2), 576 (1), 651 (0), 671 (0), 736 (9; b), 776 (1.5), 819–840 (2; db), 929 (4; b), 974 (1), 1012 (2.5), 1061 (2.5), 1133 (2.5; bg), 1179 (2.5), 1218 (4), 1227 (2), 1256 (1), 1323 (0.5), 1333 (1), 1448 (10; [illegible]), 1463 (3).
4,4,6,6-Tetramethylnonane	240 (0.3), 281 (0.8; b), 340 (1), 397 (0), 465 (0), 494 (1; db), 598 (0.5; b), 627 (0), 687 (1), 735 (8; b), 850 (1), 873 (2), 881 (0.5), [illegible], 977 (2.5), 998 (0.8), 1049 (5), 1101 (1.5 b/bg), 1133 (2), [illegible] b), [illegible] (1.5), 1263 (1), 1304 (4; b/bg), 1330 (1), [illegible] b), 1461 (2).
5,5,7,7-Tetramethylundecane	221 (1; b/bg), 320 (1.5; b), 380 (0.1), 397 (0), 420 (0), 493 (0), 550 (1; b), 575 (0.5), 696 (0), 738 (2; b), 792 (0.5), 822 (0), 834 (1.5), 875 (2.5), 893 (2), 910 (2), 939 (2.5), 994 (0), 1058 (0), 1090 (3), 1133 (1.5; b/bg), 1159 (1.5; b/bg), 1189 (4), 1241 (1), 1264 (1), 1304 (4; b), 1345 (0.5; bg), 1380 (1.5), 1408 (0.5), 1450 (10; b).

The method of combined light scattering was used to study the synthesized alkanes.

In Table 4 we give the obtained spectra with the intensities, measured on a conventional visual scale, where the intensity of the frequencies in the 1440-1450 cm^{-1} region was taken equal to 10 units.

As can be seen from the presented data, the spectra of all of the synthesized ditert-alkylmethanes show a community of intense frequencies in the regions 700-750, 930 and 1200-1250 cm^{-1}, characteristic for complex branching in the chain [7,8], i.e., for hydrocarbons with a tertiary carbon atom.

A study of the spectra also revealed that the alkanes do not contain the alkenes as impurities, since frequencies in the 1600 cm^{-1} region were absent.

Synthesis of 3,3,5,5-tetramethylheptane from ditertiary dichloride V (2,4-dichloro-2,4-dimethylheptane). The reaction of ethylmagnesium bromide (115 g of ethyl bromide, 24 g of magnesium and 200 ml of absolute ether) with the ditertiary dichloride (V) (0.25 mole) in the presence of mercuric chloride was run under the same conditions as described above for the reaction of RMgBR with the saturated tertiary monochlorides (III).

Distillation of the reaction products gave (in 5% yield, based on the dichloride) 3,3,5,5-tetramethylheptane (b.p. 71-73°/12 mm; n_D^{20} 1.4307; d_4^{20} 0.7693), and also 2,4-dimethyl-1,3-pentadiene (b.p. 92-94°/750 mm; n_4^{20} 1.4440) and its dimer (b.p. 92°/12 mm).

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ON A NEW COMPOUND IN THE SYSTEM NaF-AlF$_3$

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(Presented by Academician A. N. Frumkin, January 2, 1957)

The diagram of state of the system sodium fluoride-aluminum fluoride has been studied many times, since the cryolite (Na_3AlF_6) formed in it is the principal component in the electrolyte used to obtain aluminum electrolytically from its oxide.

In earlier investigations [1-6] it was established that in addition to cryolite the indicated system contains chiolite, whose composition according to the data of different authors is either $Na_5Al_3F_{14}$ or $Na_3Al_2F_9$.

The conclusion that only cryolite and chiolite are present in the mentioned system was supported by many investigators, despite the fact that in accord with theoretical calculations [7], based on taking into consideration the values of the ionic charges and radii in a system composed of alkali metal fluorides and aluminum fluoride, aluminum should have its most stable configuration in the equimolecular compound, having the composition $MeAlF_4$.

The existence of compounds of this type with potassium and with monovalent thallium and rubidium was established long ago [8,9]. Other than $NaAlF_4 \cdot H_2O$ [10], nothing was known about a similar compound with sodium, if we disregard the postulations relative to its possible formation in the system NaF-AlF$_3$, [11] and in the fusion of cryolite with aluminum fluoride [12], which postulations, however, were not supported by special studies [5].

The first x-ray data relating to sodium tetrafluoroaluminate ($NaAlF_4$) were published by Howard [13]; they were obtained as the result of studying the sublimates formed in the passage of one of the gases—nitrogen, hydrogen, carbon monoxide or argon—at 1000° through melts composed of sodium fluoride and aluminum fluoride.

However, it should be mentioned that not all of the values given in this paper for the interplanar distances correspond to the crystal lattice of $NaAlF_4$. Some of them belong to chiolite and aluminum fluoride. At the same time the individual values of the interplanar distances, characteristic for this compound, are not indicated. Taking this into consideration, it is impossible to accept the principal x-ray data published by Howard for $NaAlF_4$ as being fully adequate.

Independent of Howard's work, in 1954 we found the compound $NaAlF_4$ in the condensate of the sublimates obtained in the fusion of cryolite-alumina melts in an argon atmosphere at 1020°. The amount of this compound, differing from the starting substances and from chiolite and aluminum fluoride, increased with increase in the amount of AlF_3 in the melt. Its greatest amount (of the new compound) was found in the sublimates whose melts had a molar ratio of NaF to AlF_3 of 1.67 to 1.00, i.e., in the region corresponding to the so-called "acid electrolytes."

Since the condensation products of the sublimates of the indicated melts always consist of very fine powders, representing a mixture of $NaAlF_4$ and its decomposition products (chiolite and aluminum fluoride), then it can be assumed that this compound is extremely unstable under ordinary conditions and that it is only partially retained in the presence of either argon or the other gases.

For the x-ray study of the specimens obtained by us we used copper-filtered radiation in a chamber with high resolving power and a drum diameter of 143.25 mm. This made it possible to separate the maxima of chiolite and aluminum fluoride on the x-ray patterns. After they had been excluded from the inspection, the remaining unidentified maxima, characteristic for the crystal lattice of the new phase, were used for the corresponding calculations.

The calculated values of the interplanar distances, the relative intensities of the interference maxima and the indices of the reflecting planes, found by the graphical method for a tetragonal lattice, are given in Table 1.

TABLE 1

hkl	I_{exptl}	d_{exptl}, A	$I_{theoret}$	$d_{theoret}$ A	hkl	I_{exptl}	d_{exptl}, A	$I_{theoret}$	$d_{theoret}$ A
100	7	3.49	7	3.48	204	0.5	1.164	2	1.167
002	4	3.11	5	3.145	300	2	1.160	0.5	1.160
101	10	3.03	10	3.045	301	0.5	1.140	0.5	1.141
110	1	2.475	4	2.462	115	0.5	1.122	0.5	1.120
102	3	2.320	3	2.332	214	0.5	1.103	0.5	1.108
111	0.5	2.275	6	2.292	302	0.5	1.090	0.1	1.098
003	3	2.100	2	2.098	223	2	1.058	1	1.061
112	3	1.950	0.5	1.933	006	0.5	1.051	0.5	1.048
103	10	1.800	7	1.795	106	0.5	1.005	0.01	1.004
200	5	1.727	7	1.740	215	0.5	0.981	0.5	0.978
004	3	1.581	2	1.572	224	0.5	0.970	1	0.969
202	0.5	1.520	2	1.523	314	2	0.901	0.5	0.903
211	2	1.497	2	1.511	401	2	0.864	0.1	0.863
114	1	1.313	0.5	1.325	330	0.5	0.817	0.5	0.821
213	1	[illegible]	3	1.250	403	2	0.807	1	0.804
220	1	[illegible]	2	1.230	332	0.5	0.791	0.01	0.794
105	2	1.187	0.1	1.183	008	0.5	0.784	0.5	0.785

Calculation by the quadratic formula for the tetragonal system gave the lattice constants of a new compound: a = 3.48 ± 0.01 A; c = 6.29 ± 0.01 A.

The obtained data proved to be close to the constants of known lattices for compounds of the $MeAlF_4$ type. The lattice constants and the dimensions of the ionic radii for the univalent metals entering into the composition of the corresponding compounds are compared in Table 2.

TABLE 2

Compound	Lattice constants, A		Radii of the univalent ions, according to Goldschmidt, A
	a	c	
$RbAlF_4$	3.615	6.201	1.49
$TlAlF_4$	3.61	6.37	1.49
NH_4AlF_4	3.587	6.346	—
$KAlF_4$	3.55	6.130	1.33
$NaAlF_4$	3.48	6.29	0.98

To establish whether sodium tetrafluoroaluminate ($NaAlF_4$) has the same crystal lattice as its isomorphic compounds with rubidium, thallium and potassium, schematically shown in Fig. 1, we calculated the theoretical values of the intensities of the interference maxima by the formula:

$$I \sim P\frac{1+\cos^2 2\theta}{\sin^2\theta\cdot\cos\theta}\left|\sum_1^n F_s e^{2\pi i(hx+ky+lz)}\right|^2,$$

where P is the repetition factor, θ is the angle of reflection of the x-ray beams, F_s are the atomic factors of the elements entering into the crystal lattice, and xyz are the coordinates of the atoms.

For the calculations it was assumed that the $NaAlF_4$ lattice belongs to the space group $D^1_{4h} - P4/mmm$.

The z parameter for the two fluorine ions, found inside the elementary cell, was taken equal to 0.21, i.e., the same as in the lattices of the isomorphous compounds with potassium, rubidium and thallium.

The results of calculating the intensities, reduced to a 10-unit system, are given in Table 1. For comparison the theoretically calculated values of the interplanar distances are also given in the table. The obtained data show that the agreement between them is satisfactory. On the basis of this it can be assumed that sodium aluminum tetrafluoride ($NaAlF_4$) has the same crystal lattice as the indicated isomorphous compounds.

However, some attention should be given to a certain difference between the individual theoretically calculated values of the intensities and the experimental. This is explained by a superimposition of the individual maxima of chiolite, aluminum fluoride and, apparently, of another unknown compound on some of the $NaAlF_4$ interference maxima. Also not excluded is the fact that a divergence of the intensity values is determined by a distortion of the octahedron, formed by six fluorine ions, of which four are located in the centers of the sides of the tetragonal lattice.

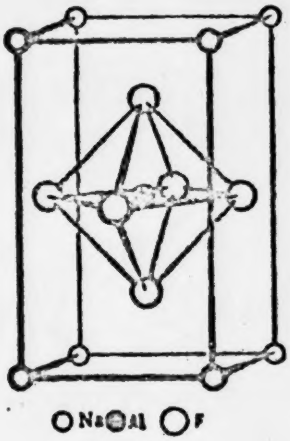

Fig. 1.

That the octahedron is distorted can be seen from the fact that the doubled sum of the radii of the trivalent aluminum ion and the univalent fluorine ion is equal 3.80 A. The crystal lattice constant a, representing the distance between the centers of the fluorine ions found on opposite faces, is equal to 3.485 A. The difference between these values (~0.3 A) indicates that the fluorine ion shows considerable polarization. This high polarization is due to a smaller value for the radius of the sodium ion (0.98 A), found in the nodes of the tetragonal lattice, when compared with the ionic radius of potassium (1.33 A). The possibility exists that this is the specific reason for the instability shown by sodium aluminum tetrafluoride under ordinary conditions when compared with the other isomorphic compounds.

Proceeding from the above, it must be assumed that the compound $LiAlF_4$ should be even less stable, since the radius of the lithium ion is equal to 0.73 A.

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THE STRUCTURE OF ORGANOCHROMIUM COMPOUNDS

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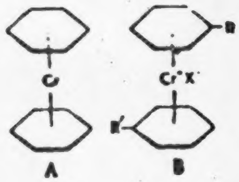
(Presented by Academician N. N. Semenov, March 8, 1957)

In a recent paper by Fischer [1] the synthesis of neutral dibenzenechromium and its salts was described and brief mention was made of several other aromatic derivatives of chromium-(O). Proceeding from x-ray structure [2], magnetochemical and spectral data [3], and also measurement of the dipole moments [4], the author postulates that dibenzenechromium-(O) has structure A, similar to ferrocene.

A number of communications [5,6] have appeared recently in which the isolation of dibenzenechromium iodide, together with the "pentaphenylchromium hydroxide" and "tetra- and triphenylchromium iodides" of Hein [7], from the [illegible] and anhydrous chromium chloride is described.



A B

Fig. 1. I) R = R' = H, X = I. II) R = H, R' = C_6H_5, X = I. III) R = R' = C_6H_5, X = I. IV) R = R' = C_6H_5, X = C_6H_5O. V) R = R' = C_3H_7-iso, X = I. VI) R = R-cyclohexyl, X = I.

According to the bold, but not rigidly proven, postulation of Zeiss [8] the polyphenyl derivatives of chromium have the general bis-arene structure B. As a result, it is expedient to adopt a single nomenclature [9] for the indicated series of compounds, in accordance with which they should be called salts of di-(π-arene)-chromium. In addition, Hein [6] is in agreement with this.

As suitable experimental proof, Zeiss used the data that he obtained in the reduction of Hein's organochromium compounds in ether medium with $LiAlH_4$, and also with $LiAlD_4$. However, in both cases these data are not very convincing. Thus, when 0.107 mmole of III was reduced with $LiAlD_4$ he isolated only 0.054 mmole of diphenyl (instead of the calculated 0.214 mmole) with a 5% content of D. From 0.70 mmole of II he obtained 0.58 mmole of diphenyl with a 6.6-6.7% content of D.

If it is assumed that in (π-benzene, π-diphenyl)-chromium and di-(π-diphenyl)-chromium iodides the diphenyl groups show covalent attachment [10], then in the diphenyl, isolated after the reaction with $LiAlD_4$, a 10% content of D should be expected; if they have the structure of B II and III, then the diphenyl should not contain any deuterium.

The composition and yield of the organic products of the photodecomposition of organochromium compounds in chloroform [11] are found to be in good agreement with the B structures. For more complete proof we ran the photolysis of III and IV in deuteriochloroform (58.2% D). The exposure of 1.250 g of tetrahydrate IV in 29.05 g of $CDCl_4$ to ultraviolet radiation (PRK-2 lamp) for 111 hours gave diphenyl in 73.3% yield and D content < 0.1%. As the result of photodecomposition (64 hours) 0.610 g of III in 28.18 g of $CDCl_3$ gave diphenyl with a deuterium content of ~ 0.3% (the error of determining D is 0.2%); the yield was quantitative. For the last reaction we postulate the following total scheme:

$$\text{III} + CDCl_3 \xrightarrow{h\nu} 2C_6H_5-C_6H_5 + CrCl_3 + I_3.$$

It is known [3,12] that the B series of compounds (I-IV) are paramagnetic and have a magnetic moment of 1.7 Bohr magnetons, which corresponds to the presence of one unpaired electron in each of their molecules. In this connection, it seemed of interest to take the spectra of the paramagnetic electron resonance of such compounds for the purpose of obtaining data on the localization of the free electron. The absorption spectrum of a water solution of III is shown in Fig. 2. The presence of a superfine structure and a qualitative analysis of the distribution of the intensities indicates that the unpaired electron reacts with the hydrogen nuclei of the aromatic rings.

Fig. 2. Absorption spectrum of a water solution of III; concentration 10^{-3} mole/liter.

A detailed discussion of these data, and also the data obtained in studying the spectra of the paramagnetic electron resonance of other compounds of this type, will be published in the near future.

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SYNTHESIS AND ANALYTICAL PROPERTIES OF THE TETRA(α-THIENYL) AND TETRA(p-ANISYL) BORATE SALTS OF THE ALKALI METALS

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(Presented by Academician A. N. Nesmeyanov, December 7, 1956)

It is known that tetraphenylborosodium [1] has recently found extensive use as a test reagent for the potassium ion. This compound also precipitates the cesium and rubidium ions. Tetraphenylboropotassium, -rubidium and -cesium show very slight solubility in water [2]. Thus, at 20° (± 0.5°) the solubility of the first salt in 100 ml of water is 0.0053 g, that of the second is 0.0018 g, and that of the third is 0.0013 g, which corresponds respectively to 0.578 mg K, 0.38 mg Rb and 0.43 mg Cs.

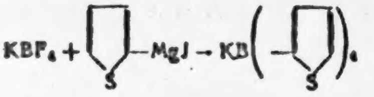
A. N. Nesmeyanov and one of us proposed a simple method for the preparation of tetraphenylborosodium [3], namely, by the reaction of phenylmagnesium bromide with sodium borofluoride:

$$NaBF_4 + C_6H_5MgBr \rightarrow NaB(C_6H_5)_4.$$

Potassium borofluoride also reacts easily with organomagnesium compounds (C_6H_5MgBr, $p\text{-}CH_3C_6H_4MgBr$ [4], $C_6H_5C \equiv CMgBr$ [5], and others) to yield the corresponding tetraaryl borate salts. It was further shown that this reaction is also possible in the heterocyclic series [6].

In this paper we describe some new potassium, rubidium, cesium and thallium salts, being of interest in analytical chemistry. Our analytical data are of a preliminary nature and show that a method for the separation of cesium from the other alkali metals, and probably a method for the quantitative determination of thallium (I), can be developed on the basis of using the tetrathienylboron anion.

The reaction of α-thienylmagnesium iodide with potassium borofluoride yields tetra(α-thienyl)boropotassium:



In contrast to tetraphenylboropotassium this salt is soluble in water. It should be mentioned that one of the important properties of tetra(α-thienyl)boropotassium is its ability to precipitate cesium and rubidium ions from water solutions:

$$KB(C_4H_3S)_4 + CsCl \rightarrow \downarrow CsB(C_4H_3S)_4 + KCl$$
$$KB(C_4H_3S)_4 + RbCl \rightarrow \downarrow RbB(C_4H_3S)_4 + KCl,$$

in which connection lithium and sodium ions do not interfere in these reactions.

A study of the solubility of the tetra(α-thienyl) borate salts of K, Rb and Cs in water as a function of the temperature gave the following data (amount of salt in grams per 100 g of aqueous solution):

	0°	15°	25°	35°	45°	60°
$KB(C_4H_3S)_4$	0.668	0.874	1.038	1.459	1.853	2.800
$RbB(C_4H_3S)_4$	0.244	0.374	0.419	0.421	0.611	1.254
$CsB(C_4H_3S)_4$	0.051	0.053	0.091	0.098	0.122	0.209

A great difference in the solubility of the potassium and cesium salts permits using tetra(α-thienyl)boropotassium to determine and separate cesium from the other alkali metals.

A solution containing 0.3 mg Cs in 1 ml still gives a positive test for cesium when treated (at room temperature) with a 1% water solution of $KB(C_4H_3S)_4$.

Tetra(α-thienyl)boropotassium quantitatively precipitates the thallium (I) ion as $TlB(C_4H_3S)_4$.

A less water-soluble salt (when compared with $KB(C_4H_3S)_4$ is obtained when potassium borofluoride is reacted with p-anisylmagnesium iodide:

$$KBF_4 + n\cdot CH_3OC_6H_4Mg \longrightarrow KB(C_6H_4OCH_3)_4$$

In our first communication [4] we described the reaction of p-anisylmagnesium bromide with KBF_4, leading to tri(p-anisyl)boron, isolated as the ammoniate. In this connection it was indicated that tetra(p-anisyl)-boropotassium is apparently formed as an intermediate reaction product. Later it was mentioned that some ammonium and pyridinium tetraaryl borate salts cannot be isolated, but instead the corresponding triarylboron ammoniates and pyridinates are formed immediately, in contrast to ammonium and pyridinium tetraphenyltungsten, which can be isolated pure. By changing the method of isolation we were able to obtain tetra(p-anisyl)boropotassium.

Tetra(p-anisyl)boropotassium is more soluble in water than is tetraphenylboropotassium, but is much more difficultly soluble than tetra(α-thienyl)boropotassium, it precipitates both rubidium and cesium ions.

The solubility (Amount of salt in grams per 100 g of water solution) of tetra(p-anisyl)boropotassium, -rubidium and -cesium in water as a function of the temperature is given in the table below:

	25°	40°	60°
$KB(C_6H_4OCH_3)_4$	0.0337	0.0553	0.166
$RbB(C_6H_4OCH_3)_4$	0.0260	0.0303	0.163
$CsB(C_6H_4OCH_3)_4$	0.0244	0.0256	0.0463

Tetra(p-anisyl)boropotassium also gives tetra(p-anisyl) borate salts with the cations of quaternary ammonium salts. Tetra(p-anisyl)boropotassium does not give the corresponding tetraaryl borate salts with ammonium and pyridinium salts, and instead the tri(p-anisyl)boron ammoniate and pyridinate are obtained respectively.

Tetra(p-anisyl)boropotassium is decomposed by dilute hydrochloric acid to di-p-anisylboric acid in 40% yield.

EXPERIMENTAL

To the α-thienylmagnesium iodide obtained from 0.93 g of magnesium, 8 g of α-iodothiophene * and

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* α-Bromothiophene can also be taken here.

40 ml of absolute ether was added 1.2 g of KBF_4. The reaction was run in a conical flask, fitted with a calcium chloride tube (a condenser was also used in the case of large amounts of reactants), with vigorous stirring. The reaction is slightly exothermic and is terminated by the separation of the mixture into layers. As soon as self-heating of the mixture had ceased and two layers had formed (in 20-35 minutes) the precipitate was filtered through a No. 1 glass filter and washed several times with absolute ether. The precipitate weighed 2.9 g. The tetra(α-thienyl)boropotassium was separated from KBF_4 by dissolving it in nitromethane. The solution was filtered and treated with absolute ether (or benzene) until a white precipitate ceased to deposit. The latter was filtered and washed with ether to give 1.3 g (36 % of theory) of tetra(α-thienyl)boropotassium. Recrystallization from water and drying in a vacuum-desiccator over P_2O_5 gave a substance with the following analysis.

Found %: C 50.07, 50.30; H 3.28, 3.28; K 10.42. $C_{16}H_{12}S_4BK$. Calculated %: C 50.25; H 3.16; K 10.23.

Tetra(α-thienyl)boropotassium is readily soluble in nitromethane and acetone, insoluble in ether and benzene, and soluble in water.

Tetra(α-thienyl)borocesium. The addition of a water solution of tetra(α-thienyl)boropotassium to a water solution of either cesium chloride or sulfate gave a precipitate of tetra(α-thienyl)borocesium, which after washing with water and drying in a vacuum-desiccator over P_2O_5 was analyzed:

Found %: C 40.33, 40.60; H 2.41, 2.50; Cs 28.01. $C_{16}H_{12}S_4BCs$. Calculated %: C 40.35; H 2.54; Cs 27.90.

Tetra(α-thienyl)borocesium is much less soluble in water than the corresponding potassium salt.

Tetra(α-thienyl)bororubidium. The addition of a water solution of $KB(C_4H_3S)_4$ to a solution of rubidium chloride gave a white precipitate of tetra(α-thienyl)bororubidium, which after washing with water and drying in a vacuum-desiccator over P_2O_5 was analyzed:

Found %: C 44.80, 44.59; H 2.76, 2.75. $C_{16}H_{12}S_4BRb$. Calculated %: C 44.82; H 2.82.

The solubility of tetra(α-thienyl)bororubidium in water is between that of the corresponding potassium and cesium salts.

Tetra(α-thienyl)borothallium (I). To a solution of 0.0512 g of thallium (I) sulfate in 20 ml of water was added in drops a solution of 0.12 g of tetra(α-thienyl)boropotassium in 40 ml of water. A white precipitate of tetra(α-thienyl)borothallium (I) deposited immediately, which was filtered, washed several times with water, and dried in a vacuum-desiccator over P_2O_5. We obtained 0.1331 g of $TlB(C_4H_3S)_4$; the calculated amount is 0.1323 g.

Found %: C 34.98, 34.76; H 2.18, 2.18. $C_{16}H_{12}S_4BTl$. Calculated %: C 35.09; H 2.21.

Tetra(p-anisyl)boropotassium. To the p-anisylmagnesium iodide, obtained from 10 g of p-iodoanisole, 1.1 g of magnesium and 100 ml of absolute ether, and decanted from unreacted magnesium, in a conical flask was added 1.34 g of finely divided KBF_4. A stopper fitted with a calcium chloride tube was used to stopper the flask. The reaction mixture was vigorously mixed for 20-25 minutes, after which it was filtered. The precipitate was washed twice with ether and air-dried. The yield of crude substance was 2.62 g. For purification the tetra(p-anisyl)boropotassium was dissolved in acetone, the solution filtered from inorganic impurities, and the salt precipitated from acetone with ether. We obtained 1.15 g (23 % of theory) of tetra(p-anisyl)boropotassium.

Found %: C 69.79, 70.01; H 5.95, 5.97. $C_{28}H_{28}O_4BK$. Calculated %: C 70.30; H 5.89.

Tetra(p-anisyl)boropotassium is a colorless crystalline substance that turns yellow when heated to about 95°, and decomposes when heated to 280-300°; it is readily soluble in acetone and pyridine, more difficultly soluble in alcohol, slightly soluble in water, and insoluble in ether, petroleum ether and benzene; it can be recrystallized from a mixture of alcohol and acetone. Water solutions of the salt give a qualitative test for K^+ with a solution of tetraphenylborosodium.

Di-p-anisylboric acid. A solution of 0.1 g of tetra(p-anisyl)boropotassium in the minimum amount of acetone was treated with several drops of dilute HCl. After 2-3 minutes the solution was treated with water. The resulting precipitate was filtered, dried in a vacuum-desiccator, and recrystallized from petroleum ether. We obtained 0.02 g (40% of theory) of di-p-anisylboric acid with m.p. 104-105° (in a sealed capillary). From the literature, m.p. 107° [7].

Tetra(p-anisyl)bororubidium. A water solution of RbCl was added to a saturated water solution of tetra(p-anisyl)boropotassium. The resulting white precipitate of tetra(p-anisyl)bororubidium was filtered, washed several times with water, and dried in a vacuum-desiccator over P_2O_5.

Found %: C 64.21, 63.98; H 5.36, 5.45. $C_{28}H_{28}O_4BRb$. Calculated %: C 64.08; H 5.38.

Tetra(p-anisyl)bororubidium is a colorless crystalline substance with fairly good thermal stability (it begins to turn yellow at 260° and decomposes above 280°); it is readily soluble in acetone and pyridine, difficultly soluble in alcohol with water, and insoluble in ether and benzene; it is precipitated from acetone solution with ether.

Tetra(p-anisyl)borocesium. A water solution of CsCl was added to a saturated water solution of tetra(p-anisyl)boropotassium. The resulting white precipitate of tetra(p-anisyl)borocesium was filtered, washed several times with water, and dried in a vacuum-desiccator over P_2O_5.

Found %: C 58.97, 59.19; H 5.06, 5.09. $C_{28}H_{28}O_4BCs$. Calculated %: C 58.77; H 4.93.

Tetra(p-anisyl)borocesium is a colorless crystalline substance (turns yellow at 270° and decomposes above 290°); it is readily soluble in acetone and pyridine, difficultly soluble in alcohol and water, and insoluble in ether and benzene; it is precipitated from acetone solution with ether.

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PHASES OF THE TUNGSTEN-BORON SYSTEM

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(Presented by Academician A. N. Frumkin, January 2, 1957)

Three borides were initially revealed in the x-ray study of the tungsten-boron system – the tetragonal W_2B and WB, and also the hexagonal W_2B_5 [1]. Later investigators established the existence of a high-temperature β-WB modification of tungsten monoboride [2,3]. According to the data of [1], W_2B (γ-phase) has very narrow limits of homogeneity, WB(δ-phase) has wider limits ranging from 48 to 51 atom % boron $WB_{0.92-1.04}$), and W_2B_5 (ε-phase) in its usual defective state is homogeneous in the limits of 66.7 to 68.0 atom % boron ($WB_{2.00-2.13}$). The WB_2 phase, established in an earlier study [4], is evidently the same as the W_2B_5 phase [illegible]th a deficiency of boron atoms.

To establish the phase regions of the tungsten-boron diagram more accurately, we* made a study of the alloys of this system by the methods of microhardness, x-ray and metallographic analyses. To prepare the alloys we used tungsten [illegible] 99 % W content (95% of the grains < 3 μ) and a preparation with tentative formula $WB_{4.75}$, obtained by the vacuum-thermal method [5] in attempting to obtain WB_x alloys with x > 5/2. The sum of the boron and tungsten in this preparation was close to 100 %. The W + $WB_{4.75}$ mixtures were composed on the basis of preparing specimens with the tentative WB_x formulas (where x = 0.01; 0.02; 0.05; 0.1; 0.2; 0.4; 0.8; 1.0; 1.5; 2.0; 2.5; 3.0), and were sintered by the method of hot pressing with subsequent prolonged annealing at 1900° and cooling from this temperature for a period of ~ 10 hours. The sintered specimens, after determining the apparent densities and hardness and studying the microstructure, were crushed to a powder and then subjected to chemical and x-ray phase analysis. The results obtained in this connection are given in Table 1.

The chemical composition of the alloys (see Table 1) hardly changed during the sintering, with the exception of the specimens with nominal composition WB_3 and $WB_{4.75}$, in which the boron content was somewhat smaller. The specimens obtained by sintering were quite dense, and after annealing the density of most of the specimens hardly changed or increased slightly; exceptions were the specimens $WB_{0.8}$, $WB_{1.5}$, $WB_{1.0}$, $WB_{2.5}$, WB_3 and $WB^4_{.75}$, where the density dropped quite sharply during annealing. This can be explained in accord with the statement of Raub and Plate [6], who indicated that the effect of the opening forces ("crystallization pressure") in the formation of intermetallic compounds is due to the individual characteristics of the newly formed particles.

A study of the microstructure of the specimens revealed that already with a boron content of 0.9 atom % the specimens begin to show two phases: one of them, light in color ("white phase"), occupies the main area of the specimen; the second, darker in color ("gray phase"), is located at the interstices of the polyhedrons of the white phase. With increase in the boron content the amount of the gray phase increases, and with an alloy content of 16.69 atom % B the grains of the gray phase occupy up to 40% of the specimen area. The white phase, apparently representing a solid solution of boron in tungsten, has a hardness of 550-770 kg/sq. mm., remaining practically constant with change in the alloy composition up to 28.68 atom % B. The hardness of the gray phase, the boride W_2B is 2420 ± 120 kg/sq. mm. With further increase in the boron content of the alloys from 33.3 to 50 atom % the WB phase appears, the hardness of which increases from ~ 280 to ~ 3700 kg/sq. mm. in these limits for the boron concentration.

Increasing the boron content up to 60 atom % and higher causes a dark-gray phase to appear, with a hardness that increases uniformly from 1764 kg/sq. mm. (at 66.7 atom % B) to 2599 kg/sq. mm. (at 81.4 atom % B in the alloy). The maximum hardness of this phase is in good agreement with the hardness shown by W_2B_5 [7]. Apparently, this phase has a wide homogeneous region (from 66.7 to 75-77 atom % B), since the WB_2 specimen appears as a single phase, while the second phase, lighter in color, appears only in the specimen with a B content of 75.0 atom % (15.24 wt. %). The latter has a hardness of 3600 kg/sq. mm., which is close to the hardness of boron [8].

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* S. D. Krasnenkova participated in the work.

TABLE I

Calculated composition			Actual; mt. of B in sintered spec., wt. %	Calculated density	Density		Microhardness, kg/sq. mm		Phase composition	Periods of the phase lattices, A			
WB_x	B, wt. %	B, atom %			after hot pressing	after annealing	white phase*	gray phase*		W	W_2B	WB	W_2B_5
W	–	–	–	19.3	19.00	19.00	350	–	W	3.149			
$WB_{0.01}$	0.050	0.6	0.055	–	18.00	17.88	700 ± 98	–	$W + W_2B$	3.133	5.565	–	–
$WB_{0.02}$	0.118	1.9	0.115	–	18.3	17.95	622 ± 60	–	$W + W_2B$	3.133	5.60	–	–
$WB_{0.05}$	0.294	4.75	0.290	–	17.90	18.23	640 ± 78	–	$W + W_2B$	3.132	5.600	–	–
$WB_{0.1}$	0.586	9.31	0.573	–	17.78	17.83	556 ± 43	–	$W + W_2B$	3.130	5.550	–	–
$WB_{0.2}$	1.156	16.63	1.19	–	16.94	17.24	772 ± 167	2400 ± 161	$W + W_2B$	3.130	5.547	–	–
$WB_{0.4}$	2.30	28.6	2.25	–	16.94	17.61	749 ± 163	2500 ± 103	$W + W_2B$	3.133	5.562	–	–
$WB_{0.5}$	2.86	33.3	2.88	16.72	16.7	16.71	–	2420 ± 120	W_2B	–	5.561	–	–
$WB_{0.8}$	4.70	44.4	4.29	–	16.60	14.61	–	2084 ± 193	$(W_2B) + WB$	–	5.550	3.124	–
$WB_{1.0}$	5.56	50.0	5.45	16.0	16.70	14.08	–	3732 ± 176	$(W_2B) + WB$	–	–	3.131	–
$WB_{1.5}$	8.11	60.0	8.15	–	15.85	13.65	–	3774 ± 457	$WB + (W_2B_5)$	–	–	3.132	2.980
$WB_{2.0}$	10.52	66.7	10.20	–	15.04	13.00	–	1704 ± 103	$(WB) + W_2B_5$	–	–	3.130	2.976
$WB_{2.5}$	12.8	71.4	12.70	13.1	13.00	11.05	–	2050 ± 200	W_2B_5	–	–	–	2.980
$WB_{3.0}$	13.95	75.0	12.95	–	12.70	11.20	–	2704 ± 150	W_2B_5	–	–	–	2.981
$WB_{4.375}$	20.37	81.4	15.24	–	12.46	11.60	3600 ± 90	2500 ± 120	$B + W_2B_5$	–	–	–	2.983

The data of the metallographic study are well supported by the x-ray analysis results. The lattice period of the tungsten powder, used in the study, was 3.149_3 A, which is in quite close agreement with recent literature data [9]. When 0.6 atom % B is added to the tungsten the period drops slightly (to 3.133 A), after which it remains practically constant up to a boron content of 28.6 atom %. All of these alloys are two-phase in nautre – the second phase is the boride W_2B with the periods a = 5.564 A and c = 4.729 A, which coincides exactly with the data of Kiessling [1]. The alloys $WB_{0.8}$ and $WB_{1.0}$ are one-phase in nature, if the presence of individual very weak W_2B lines on the x-ray pattern of $WB_{0.8}$ is neglected, and represent the boride WB with periods, increasing, for example, along the a axis from 3.124 to 3.131 A. This boride is also observed in the alloys $WB_{1.5}$ and WB_2, but in the form of a few weak lines on the x-ray patterns. Beginning with the composition $WB_{1.5}$, the principal phase is the boride W_2B_5 with maximum period a = 2.983 A (according to Kiessling, 2.982 A). In addition to the W_2B_5 lines, the lines for boron are observed in the specimen with a B content of 75.0 atom %, shown by comparison with the interplanar distances obtained by the use of the data of [10].

On the basis of the obtained data it can be stated that the following phase regions exist in the tungsten-boron system (from 1 to 70-80 atom % B):

1) an α-region of very limited solid solution of boron in α-W, formed with a reduction in the lattice period and a corresponding distortion, leading to an increase in the hardness from 340 to 550-770 kg/sq. mm.;

2) a two-phase region of α + γ, in which connection the γ-phase (W_2B) shows a very narrow homogeneous region and a hardness of 2420 kg/sq. mm.;

3) a two-phase region of $\gamma + \delta$ ($W_2B + WB$);

4) a homogeneous region of WB (δ-phase), extending at the most from 44.4 to 50-53 atom % B, with a hardness, changing within these limits, of 2030 to 3732 kg/sq. mm.;

5) a two-phase region of $\delta + \epsilon$ ($WB + W_2B_5$);

6) a homogeneous region of W_2B_5, probably quite wide and extending from 63 to 73 atom % B, which does not agree with the earlier data of Kiessling [1] that W_2B_5 is either absent or is present only in a very narrow homogeneous region. Evidently, the phase containing less than 71.4 atom % B is formed on the principle of substracting boron atoms, and the phase containing more than 71.4 atom % B on the principle of adding boron atoms.

The comparatively low hardness shown by the γ-phase (W_2B) is associated with the isolated position of the boron atoms in the elementary cell, whereas the maximum hardness is shown by the δ-phase (WB), where the boron atoms are linked in zigzag chainlets. The hardness of the ϵ-phase (W_2B_5) is somewhat lower than that of the δ-phase, probably due to the formation of layers of boron atoms, making the alloy more inclined to shift-deformation, all the more so since the ϵ-phase can be regarded as having a simple hexagonal lattice with the boron atoms in its interstices.

In addition, the W_2B_5 phase does not show a high order to regularity, which appears, in particular, in its ability to form broad regions of solid solutions with other borides as the solvent [11].

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THE PHOTOCHEMICAL SULFOXIDATION OF n-HEPTANE WITH SULFUR DIOXIDE GAS AND OXYGEN

Academician A. V. Topchiev, G. M. Tsiguro and G. V. Gryaznov

The direct sulfonation of n-heptane with either sulfuric acid or oleum is not very effective. n-Heptane reacts with fuming sulfuric acid to yield only traces of heptanesulfonic acids [1]. They are also formed in the sulfoxidation of n-heptane with sulfur dioxide and oxygen in the presence of organic peracids [2]. The purpose of the present study was to investigate the direct photochemical sulfoxidation of n-heptane in the liquid phase.

The sulfoxidation of n-heptane was run at 20° in a vertical quartz tube with a 30-mm diameter, fitted at the top with a reflux condenser. Through the hydrocarbon, charged into the tube in 300-400 ml amount, was bubbled an equimolar mixture of sulfur dioxide and oxygen, dispersed into fine bubbles by means of a capillary in the tube through which the gases were admitted. Ultraviolet light with a wave length of 3650 A was used to illuminate the reaction [illegible] mercury-quartz burner was installed vertically at a distance of 125 mm from the reactor. During [illegible] reaction products which collected in the lower portion of the tube were separated from the hydrocarbon layer.

In all of our experiments the yield of reaction products was independent of the concentration of sulfur dioxide and oxygen in the gas mixture and was directly proportional to the time of their passage through the n-heptane layer, which indicates that the yield is proportional to the number of light quanta absorbed by the reactants. The degree to which the sulfur dioxide and oxygen are utilized is linearly proportional to the height of the hydrocarbon layer through which the gases are bubbled.

The reaction products that separated from the hydrocarbon layer and collected in the lower portion of the quartz tube represented a mixture of substances, the composition of which is given in Table 1.

TABLE 1

Composition of the Products of the Photochemical Sulfoxidation of n-Heptane

Substance formula	$C_7H_{15}SO_3H$	$C_7H_{14}(SO_3H)_2$	$C_7H_{15}OH$	H_2SO_4
Amount in wt. %	67	5-6	5-9	18

The rate at which the reaction products separate is not appreciably influenced by the prior addition of benzoyl peroxide to the n-heptane. Apparently, the investigated process does not have an induction period. In the presence of toluene, which, according to our studies, is inert to photochemical sulfoxidation by gaseous sulfur dioxide and oxygen, in either the liquid or the vapor phase, the sulfoxidation of n-heptane was practically nil. It was established that n-heptane under these conditions induces the oxidation of toluene, whereas even a trace amount of either the latter or its oxidation products inhibits the photochemical sulfoxidation of n-heptane.

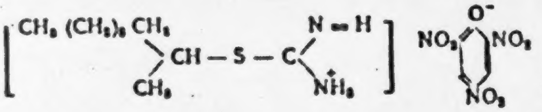
The results of the experiments, run by us in a flow system, revealed that the photochemical sulfoxidation of n-heptane by gaseous sulfur dioxide and oxygen is a consecutive reaction, proceeding with the intermediate formation of mono- and disulfinic acids. We were able to obtain these acids in the process of bubbling sulfur dioxide through n-heptane in the presence of radiation by ultraviolet light. The heptanesulfinic acids are readily soluble in n-heptane and in this solvent are easily oxidized by oxygen to give the heptanesulfonic acids, which separate from the hydrocarbon and do not contain sulfuric acid. In a special series of experiments, run in a stationary closed system, it was experimentally established that the photochemical sulfoxidation of n-heptane proceeds with the intermediate formation of heptanesulfinic acids.

To determine the structure of the heptanemonosulfonic acid, the latter, together with the heptanedisulfonic acid, were separated from sulfuric acid by the salt method as the barium salts, the subsequent treatment of which with phosphorus pentachloride gave a mixture of the mono- and disulfonyl chlorides. This mixture was dissolved in an equal volume of dry isopentane, the solution cooled in a Dewar vessel to -54°, and then the precipitated heptanedisulfonyl chloride, difficultly soluble even in warm isopentane, was filtered at this temperature. The filtrate after removal of the solvent represented a mixture of 64 wt. % monoheptanesulfonyl chloride and 36% heptyl chloride, apparently formed principally in the process of obtaining the chlorides of the heptanesulfonic acids, due to reaction with phosphorus pentachloride [3]:

$$C_7H_{15}SO_2Cl + PCl_5 \rightarrow C_7H_{15}Cl + SOCl_2 + POCl_3.$$

The heptanemonosulfonyl chloride was subjected to thermal desulfonation at 195-200°. Here we obtained 2-chloroheptane which distilled at 146-149° and had refractive index n_D^{23} 1.4212 (from literature, b.p. 147-150° and n_D^{23} 1.4222 [4]).

In addition to identification by the physicochemical constants, we obtained the crystalline S-heptylisothiourea picrate, having [illegible]-117°, from the isolated heptyl chloride by the method of Levy, Brown and Campbell [5].



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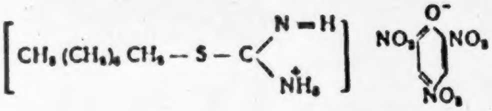
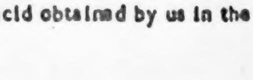
The picrate was prepared in the following manner. A solution of 0.5 g of thiourea in 5 ml of 95% ethyl alcohol was treated with 0.63 g of heptyl chloride. The obtained solution was boiled under reflux for 1 hour, after which 0.5 g of picric acid with m.p. 120.9-121° was added, and the boiling continued for another 10 minutes. The alcohol solution after cooling was diluted with 45 ml of distilled water, and here the formed picrate crystallized as yellow leaflets, which were suction-filtered and recrystallized from 50% methyl alcohol.

A mixture of the obtained picrate with the picrate, prepared in the same manner from n-heptyl bromide and having m.p. 127-127.5°,



melted at 110.5-111.5°.

As a result, the heptanemonosulfonic acid obtained by us in the photochemical sulfoxidation of n-heptane is α-methylhexanesulfonic acid



$$\begin{array}{l} CH_3(CH_2)_4CH-SO_3H \\ \qquad\qquad\quad | \\ \qquad\qquad\; CH_3 \end{array}$$

From the potassium salt of the heptanesulfonic acid, obtained by treating the barium salt with an equimolar amount of potassium sulfate, we synthesized the previously unknown benzylthiuronium salt of the heptanesulfonic acid. This synthesis was performed as follows. A solution of 1.16 g (0.0053 mole) of the potassium heptanesulfonate in 4 ml of distilled water was cooled in ice and then mixed and shaken well with an ice-cooled solution of 1.32 g (0.0065 mole) of benzylthiuronium chloride (m.p. 173-174°) in a small amount of water. Crystals of the benzylthiuronium salt of the heptanesulfonic acid deposited on cooling; these were collected on a filter and washed with cold water. Repeated recrystallization from 50% ethyl alcohol gave the product as scaly crystals, having m.p. 105.5-106.5°.

It is indicated in the literature that the photochemical sulfoxidation of paraffin and cycloparaffin hydrocarbons proceeds by a chain mechanism. Thus, Graf [6] and Orthner [7] believe that this reaction is a chain reaction and that it proceeds with the intermediate formation of alkanepersulfonic acids, which in water solution are instantly reduced by sulfurous acid to the alkanesulfonic acids, giving an equimolar amount of sulfuric acid

$$RSO_2O_2H + SO_2 + H_2O \rightarrow RSO_3H + H_2SO_4. \qquad (1)$$

The formation of sulfinic acids observed by us, and also the much greater amount of heptanesulfonic acids in the reaction products when compared with the amount of sulfuric acid that should have been obtained in accord with this scheme, do not support the formation of heptanesulfonic acids and sulfuric acid as the result of decomposing the heptanepersulfonic acids with sulfurous acid in accord with equation (1). The formation of sulfuric acid by equation (1) is in general of slight probability in our experiments, due to the fact that the water, needed for this reaction to proceed, could have been introduced into the reaction medium in extremely minute quantities together with the reaction gases. As indicated by Graf [6], water can originate as the result of the reaction

$$C_nH_{2n+1}SO_2O_2H + C_nH_{2n+2} \rightarrow C_nH_{2n+1}SO_3H + C_nH_{2n} + H_2O, \qquad (2)$$

but we failed to observe any appreciable formation of unsaturated compounds in our experiments.

We believe that the photochemical sulfoxidation of n-heptane with gaseous sulfur dioxide and oxygen is a consecutive reaction, proceeding the following manner. n-Heptane reacts with a sulfur dioxide molecule, activated by ultraviolet light, to yield a heptanesulfinic acid

$$SO_2 + h\nu \rightarrow SO_2^{*}. \qquad (3)$$

$$C_7H_{16} + SO_2^{*} \xrightarrow{h\nu} C_7H_{15}SO_2H. \qquad (4)$$

This process of forming and accumulating heptanesulfinic acids is the slow step of the reaction. In the presence of oxidizing agents, which under our experimental conditions can be both molecular and atomic oxygen, and also ozone, there occurs the continuous oxidation of the heptanesulfinic acids to heptanesulfonic acids, which then separate from the hydrocarbon:

$$2C_7H_{15}SO_2H + O_2 \rightarrow 2C_7H_{15}SO_3H, \qquad (5)$$

$$C_7H_{15}SO_2H + O^{\cdot} \rightarrow C_7H_{15}SO_3H, \qquad (6)$$

$$C_7H_{15}SO_2H + O_3 \rightarrow C_7H_{15}SO_3H + O_2. \qquad (7)$$

Simultaneously with the described consecutive reaction the formation of heptanesulfonic acids from eptanepersulfonic acids in accord with scheme (1) can also proceed to some degree. In addition to this process, sulfur trioxide is also apparently formed under our experimental conditions as the result of the oxidation of sulfur dioxide by n-heptane hydroperoxide,

$$C_7H_{16} + O_2^{*} \rightarrow C_7H_{15}OOH, \qquad (8)$$

$$C_7H_{15}OOH + SO_2 \rightarrow C_7H_{15}OH + SO_3. \qquad (9)$$

The presented scheme, although not final, nevertheless permits making a more complete interpretation of the experimental data. The experimental data obtained by us are insufficient to establish the mechanism of the photochemical sulfoxidation of aliphatic hydrocarbons by gaseous sulfur dioxide and oxygen, and additional special studies are needed. Studies in this direction are being continued.

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STUDY OF THE STRUCTURE OF HYDROXAMIC ACIDS AND SOME OF THEIR DERIVATIVES BY THE METHOD OF INFRARED SPECTROSCOPY

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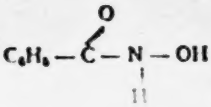
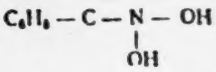
(Presented by Academician A. N. Nesmeyanov, November 16, 1956)

A fairly good study has been made of the properties of the benzohydroxamic acids, but the question as to their chemical structure still lacks an adequate answer. Up to the present time a dual structure has been assigned to them in the chemical literature. For example, monobenzohydroxamic acid is assigned two structures:

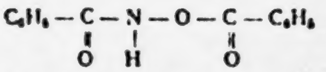

(I)



$C_6H_5-C-\underset{\underset{OH}{|}}{N}-OH$

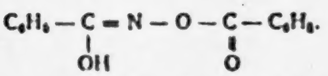
(II)

and correspondingly, dibenzohydroxamic acid is assigned the structures:



$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-O-\underset{\underset{O}{\|}}{C}-C_6H_5$

(III)



$C_6H_5-\underset{\underset{OH}{|}}{C}=N-O-\underset{\underset{O}{\|}}{C}-C_6H_5.$

(IV)

The picture is even more obscure relative to the structure of the acyl derivative of dibenzohydroxamic acid-tribenzohydroxylamine, which exists as two crystalline α- and β-modifications with different melting points and a different solubility. Some authors [1-3] believe that these modifications of tribenzohydroxylamine represent physical polymorphs, while others relate them to tautomeric substances, existing as the hydroxamic and hydroximic forms, in which connection not one of the authors indicates which structure can be assigned to which modification of the tribenzohydroxylamine.

TABLE 1

Expt. No.	r_p (C_6H_6)	$r_{p+\beta}$	$r_{p+\beta+\alpha}$	$\Delta\beta$	$\Delta(\beta+\alpha)$	Depression, °C
1	4.885	4.479	4.444	0.406	0.441	0.035
2	4.1515	4.104	4.076	0.411	0.439	0.028
3	4.500	4.001	4.055	0.409	0.445	0.036

To answer the question as to whether the α- and β-forms of tribenzohydroxylamine are physical polymorphs or chemical isomers, we made a study of the possibility and conditions for their mutual transformation, and we also made a study by the Sidgwick method and measured the dipole moments.

Interconversion was not observed for the α- and β-forms when they were heated and then cooled. Under the influence of nitrogen-containing solvents (pyridine, nitrobenzene, aniline, quinoline) a transition of the less stable β-form into the more stable α-form of tribenzohydroxylamine was observed. The reverse transition of the α-form into the β-form could not be shown under any conditions.

This study permits making the preliminary conclusion that the α- and β-forms of tribenzohydroxylamine are not polymorphic substances. The results of determining the cryoscopic lowering of the melting points by the Sidgwick method [4] are given in Table 1.

The depression produced by the addition of the α-form to a saturated solution of the β-form was on the average 0.033°. A substantial increase in the depression is evidence that the α- and β-forms of tribenzohydroxylamine represent isomeric substances.

Measurement of the dipole moments of the α- and β-forms of tribenzohydroxylamine, made by the dilute solution method [5], and calculation by the Guggenheim method [6], revealed a substantial difference in the dipole moments of the investigated forms. Thus, the dipole moment of the α-form proved to be equal to 3.78 D, and that of the β-form to 4.84 D. Such a difference in the values of the dipole moments supports the previous conclusions that the α- and β-forms of tribenzohydroxylamine are isomers.

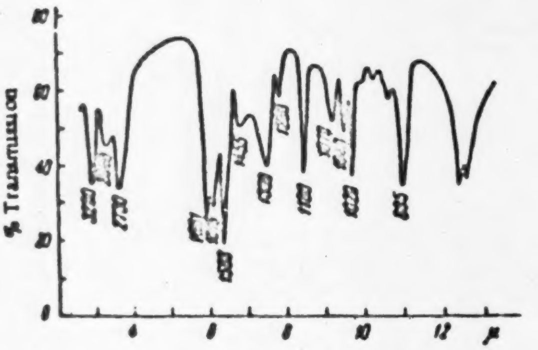


Fig. 1.

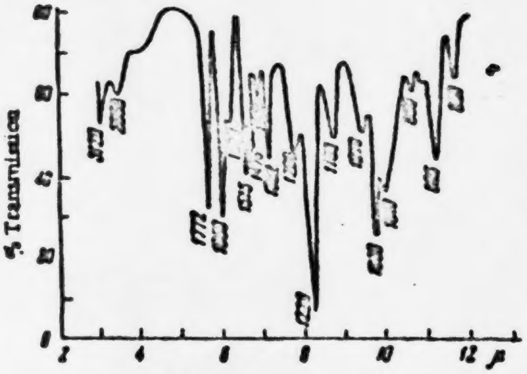
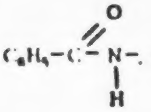
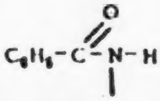


Fig. 2.

To elucidate the structure of the benzohydroxamic acids and of the α- and β-forms of tribenzohydroxylamine in the crystalline state we made a study of the absorption spectra of these substances in the infrared region of the spectrum from 2.5 to 13μ, using an IKS-11 infrared spectrophotometer. In the spectrum of the monobenzohydroxamic acid (Fig. 1) an intense band at 1661 cm⁻¹ is typical for monosubstituted amides [7] and testifies to the presence of the  $C_6H_5-\overset{O}{\overset{/\!/}{C}}-\underset{H}{\underset{|}{N}}-$ grouping in the molecule. In the high-frequency region there are frequencies at 3280 and 2730 cm^{-1}, which, apparently, belong to the vibrations of the NH- and OH-bonds. On the basis of the presented data it can be assumed that the structure of monobenzohydroxamic acid in the crystalline state can most probably be expressed by formula (I). In the dibenzohydroxamic acid spectrum (Fig. 2) in the 1600-1750 cm^{-1} region there are present two highly intense bands at 1650 and 1772 cm^{-1}. The high intensity and position of these bands permits relating them to the vibrations of the CO-groups in the molecule. The band at 1650 cm^{-1} is characteristic for monosubstituted amides, and, the same as for the monobenzohydroxamic acid (1661 cm^{-1}) testifies to the presence of the  $C_6H_5-\overset{O}{\overset{/\!/}{C}}-\underset{|}{N}-H$ grouping in the molecule. In our opinion, the band at 1772 cm^{-1} is determined by the carbonyl ester grouping. An increase in this frequency (CO) is determined by the presence of a bond between the ester group (through oxygen) and the nitrogen atom with an unshared pair of electrons. The band at 3120 cm^{-1} belongs to vibration of the NH-bond, participating in vigorous intermolecular reaction. As a result, it must be assumed that dibenzohydroxamic acid in the crystalline state has structure (III).

A comparison of the infrared absorption spectra of the α- and β-forms of tribenzohydroxylamine (Figs. 3 and 4) reveals a great difference between them. This again testifies to the fact that the investigated substances are isomeric compounds.

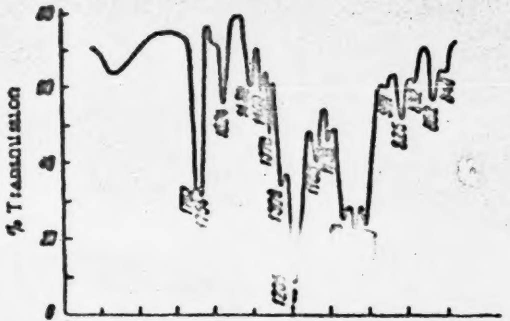


Fig. 3.

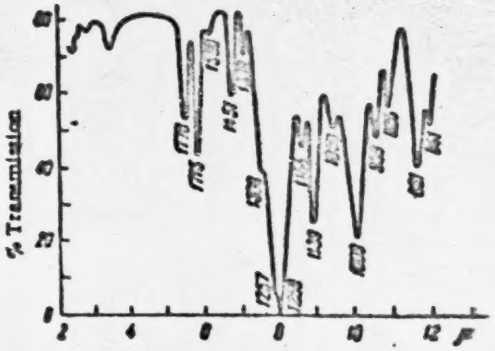
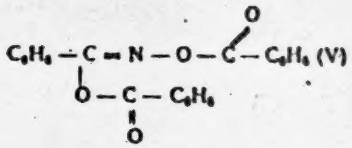


Fig. 4.

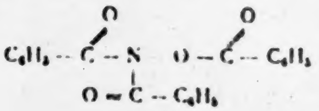
In the spectrum of the β-form (Fig. 3) in the double bond region there exist three absorption bands: two very intense bands at 1762 cm^{-1} and 1754 cm^{-1}, and a third weak band at 1624 cm^{-1}. Based on the considerations presented above, the band at 1762 cm^{-1} can be related to the ester grouping, bound through oxygen with the nitrogen atom, while the band at 1754 cm^{-1} can be related to the ester grouping linked to the carbon atom. Because of its weak intensity and low frequency value the band at 1624 cm^{-1} most suitably characterizes the C=N frequency [8, 9]. Proceeding from these data, the β-form of tribenzohydroxylamine can be assigned the hydroximic structure:



$$C_6H_5-\underset{\underset{\overset{\|}{O}}{O-C-C_6H_5}}{C}=N-O-\overset{O}{\overset{\diagup}{C}}-C_6H_5 \quad (V)$$

In the spectrum of the α-form (Fig. 4) of tribenzohydroxylamine in the region of the carbonyl frequencies there exist two absorption bands. The band at 1776 cm^{-1}, the same as in the cases examined above, characterizes the ester linkage of the carbonyl group in the ester grouping, linked through oxygen with the nitrogen atom. The intense band at 1715 cm^{-1} is the C=O amide band. An increase in this frequency is explained by the fact that electronegative groups are linked with the nitrogen atom [10].

No bands whatsoever were found in the double bond region (1620-1640 cm^{-1}). As a result, the α-form of the molecule can be assigned the hydroxamic structure (VI):



$$C_6H_5-\overset{O}{\overset{\diagup}{C}}-\underset{O=C-C_6H_5}{\underset{|}{N}}\quad O-\overset{O}{\overset{\diagup}{C}}-C_6H_5$$

I consider it my duty to thank Yu. N. Sheinker for his guidance and assistance in the execution of this study.

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